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HETEROGENEOUS EQUILIBRIA BETWEEN AQUEOUS
AND METALLIC SOLUTIONS
THE INTERACTION OF MIXED SALT SOLUTIONS
AND LIQUID AMALGAMS
A STUDY OF THE IONIZATION RELATIONS OF POTASSIUM
AND STRONTIUM CHLORIDES IN MIXTURES

BY

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I HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER MY SUPER-
VISION BY EDWIN ARTHUR REES

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Edwin A. Rees.



1. INTRODUCTION.

1. PURPOSE OF THE INVESTIGATION. This investigation is the fifth of the series being carried out in this laboratory with the object of studying the ionic relationships which exist in aqueous solutions of mixed strong electrolytes, particularly in the region of "concentrated" solutions. The present work comprises a study of the mixed chlorides of potassium and strontium in concentrations ranging from .05N to 3.00N. The method employed is based upon a distribution equilibrium of the two molecular species, potassium and strontium, between two non-miscible phases, water and mercury, as originally developed by G.McP.Smith(1)(2)(3)(4)(5).

2. PRINCIPLES RELATING TO THE IONIZATION OF SALTS.

Van't Hoff has shown that the colligative properties of dilute solutions are intimately connected by a set of relations which must of necessity follow from the two Laws of Thermodynamics (6). These relations may now in general be applied to all Solutions of Constant Thermodynamic Environment (7) (8). The failure of the application of these principles to the more general class of solutions, those of Variable Thermodynamic Environment, may be attributed to the occurrence of complex chemical processes between the different molecular species in the solution, the extent of the magnitude of which is unknown quantitatively.

The anomalous behaviour of van't Hoff's generalizations when applied to the particular class of solutions of Variable Thermodynamic

2.

Environment with which this paper deals, namely those which conduct electricity, led Arrhenius to propose the Ionic Theory (9). Any successful theoretical interpretation of the behaviour of solutions of electrolytes can now be made only in the light of this theory and it involves necessarily a knowledge of the concentrations of the different ionic species present.

Even in solutions of single electrolytes, there is no strict agreement in the degrees of ionization obtained in solutions as dilute as 0.10N by the different methods available, namely those involving colligative properties and the Arrhenius conductivity method. However, the conductance ratio, $\frac{\Lambda}{\Lambda_0}$, Λ corrected if necessary for viscosity, has been considered the reliable method of measuring the degree of ionization of at least uni-univalent electrolytes, but only in dilute solutions (7).

The conductivity study has been extended to mixtures of salts and data is on hand for every possible combination of uni-univalent, uni-bivalent, bi-univalent, and bi-bivalent types from the work of Arrhenius (10), Barnwater (11), MacGregor, Archibald, McIntosh and McKay (12), M.S. Sherrill (13) and C. Sandonni (14). Salts with no common ion, with a common anion and with a common cation have been studied and Barnwater has even extended the study to mixtures of three and four electrolytes. And in all cases, with only slight deviations, it has been found that the measured specific conductance of the mixture agrees fairly well with the specific conductance as calculated additively from the measured specific conductances of the separate salts, assuming that the conductance of each electrolyte in the mixture is the same as it is in a pure solution of the electrolyte at the same equivalent concentration. Solutions of this type were called Isohydric Solutions by Arrhenius.

For the uni-univalent electrolytes then, where conductivity may be regarded as a measure of ionization, we may state what is known as the Isohydric Principle: namely, that the degree of ionization of each electrolyte in the mixture is equal to the value which that electrolyte has in its own pure solution at the same equivalent concentration. G.McP.Smith and T.R.Ball (4) have studied mixed NaCl and KCl solutions in equivalent proportions by means of the distribution equilibrium between water and mercury and found that the ion fraction of potassium is in all cases less than that of sodium, although from the Isohydric Principle it should be somewhat greater.

G.M.J.McKay(15) made transference experiments with mixed solutions of KCl and K_2SO_4 , 0.2009N with respect to each salt. Under the assumption that the transference number of the chlorine in the KCl in this mixture is the same (.504) as it is in dilute KCl solutions, the proportion of the current carried by its ions was found to be .573 and the proportion carried by the ions of K_2SO_4 to be .427. By multiplying these values by the measured specific conductance of the mixture, the partial specific conductance of the KCl was found to be 2% larger and that of K_2SO_4 5.2% smaller than the values calculated on the basis of the Isohydric method of Arrhenius. But nevertheless, the observed conductance of the mixture differed from the sum of the partial conductances by only about 1%.

Even for solutions of single salts of the uni-bivalent type, there is no very satisfactory method of ascertaining the ion concentrations. Harkins (16) has offered approximate calculations by applying a variety of estimations from conductivity methods to fairly dilute solutions.

It seems then that the usual methods of studying ionization, colligative property and conductance methods, offer no satisfactory

evidence concerning the ion relationships of strong electrolytes, either singly or in mixtures , in the region of concentrated solutions.

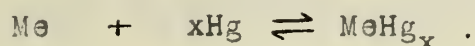
II. HISTORICAL.

1. CONSTITUTION OF THE MERCURIAL PHASE. The solid crystalline amalgams of the alkali and alkali earth metals have long been regarded as definite chemical compounds (cf.17). But ever since Prof. Ramsay determined the molecular weight of many metals by the method of measuring the change in vapor pressure when certain known weights of solid metals were dissolved in mercury, the view has persisted more or less that the liquid amalgams were mercurial solutions of these metals in the monatomic condition (18). It was some fifteen years later before definite evidence as to the contrary was substantiated.

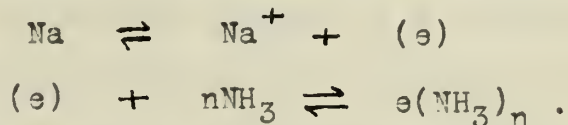
Le Blanc (19) regarded the ammonium amalgam as a compound of the metallic-like radical, ammonium, with mercury but Moissan (20) thought it was a simple or double ammoniacal hydride of mercury and Rich and Travers (21), by a series of cryoscopic measurements, thought they had proved it to be simply a solution of free ammonium in mercury. The question was settled beyond dispute in 1907 by G.McP.Smith (22), who showed that the conception of LeBlanc was correct and that ammonium amalgam must be regarded as a solution of a compound of the general formula, MeHg_x , in mercury. Similar views were advanced by G.McP.Smith (23)(24) in regard also to the amalgams of the alkali and alkali earth metals. Additional evidence substantiating these ideas was shown later (25)(26)(27)(28), and Beckmann and Liesche (29) have reached the same conclusions from cryoscopic measurements.

From a study of e.m.f. and vapor pressure measurements, J.H.Hildebrand (30) has drawn the conclusions that thallium amalgam contains TlHg_6 and breaks down into a simpler compound, probably TlHg_2 , in the more concentrated solutions; that indium amalgam contains InHg_4 , which also breaks down and that cadmium amalgam ^{contains} free cadmium and the compound, CdHg , in equilibrium.

There can then be no further doubt as to the existence of hydrargyrides in mercurial solutions, and the liquid amalgams of the alkali and alkali earth metals must be regarded as solutions of the solid amalgams in mercury. And as the amalgamated metal possesses a certain tendency to enter solution in the ionic condition, the mercurial compound must be partially dissociated as shown by the equilibrium

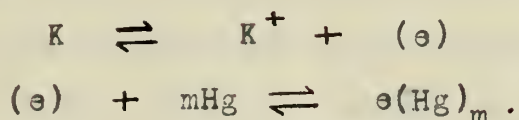


In the light of this discussion on the constitution of amalgams, it is interesting to note some recent work on the electrical transference of amalgams by G.N.Lewis (31). According to the theory of Kraus (32), when a metal is dissolved in a non-metallic solvent, as sodium in liquid ammonia, it dissociates into a positive sodium ion and an electron, which may be in part combined with the molecules of the solvent. The equilibrium may be represented as follows:



An ammoniation of the electrons would increase with dilution and we should expect the negative carrier to move more rapidly in dilute than in concentrated solutions. This fact was observed by Kraus. Lewis applied this theory of Kraus to the mercurial solutions and considers dilute sodium and potassium amalgams as composed of small

regions whose centers are sodium or potassium atoms embedded in a mass which has all the properties of mercury. A similar equilibrium might be written:



2. PREVIOUS INVESTIGATIONS ON INTERACTIONS BETWEEN LIQUID AMALGAMS AND SALT SOLUTIONS. In 1808, Seebeck made the interesting discovery that when mercury is brought into a strong aqueous solution of ammonia and an electric current passed through it, the metal increases rapidly in bulk, giving rise to an amalgam-like mass. The same observation was made almost simultaneously by Berzelius and Pontin, whilst Davy, as soon as he was informed of the fact, repeated the experiment and discovered that a piece of sal-ammoniac, moistened with water, might be employed instead of aqueous ammonia. Davy also noticed that the same amalgam-like mass is formed when an amalgam of potassium is thrown into a concentrated solution of sal-ammoniac (33). This seems to be the earliest recorded observation on the interaction of salt solutions and liquid amalgams.

Then in 1834, R. Boettger prepared dilute amalgams of barium and strontium by the action of saturated solutions of their chlorides on sodium amalgam (34) and in 1862, C.W. Vincent prepared chromium amalgam by the addition of sodium amalgam to a solution of chromium chloride and after distillation of the mercury, he obtained metallic chromium (35). This method of obtaining the free metals was later applied to manganese and cobalt by W.B. Giles (36) and Crookes (37) stated just a little later that salts of most of the heavy metals and also those of the alkaline earths could be reduced to the metallic state by this method.

In 1871, Kraut and Popp (38) obtained crystals of potassium amal-

gam by allowing a sodium amalgam to stand for several days under a strong solution of potassium hydroxide or potassium carbonate and then in 1891, J. Schumann (39) continued the study of the action of dilute sodium amalgam upon different salt solutions and succeeded in preparing amalgams of barium, cobalt, copper, magnesium and manganese.

Six years after the proposal of the ionic theory, Svannte Arrhenius (40), in electrolyzing aqueous solutions of salts of alkali metals with mercury cathodes, observed that some time elapsed before hydrogen was given off from the amalgam formed at the cathode. He attributed this to the presence of ions of sodium or potassium in the solution which would hinder the entrance of more of these metals into solution to form ions. This was the beginning of the establishment of a theoretical basis for the explanation of the different phenomena which had been observed in the interaction of amalgams and salt solutions.

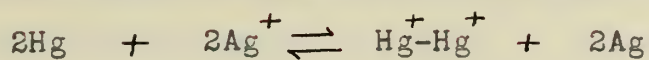
The developement of a firm theoretical basis for such reactions is due primarily to Nernst (41), who applied the expression

$$\sqrt[n_1]{\frac{P_1}{p_1}} > \sqrt[n_2]{\frac{P_2}{p_2}}$$

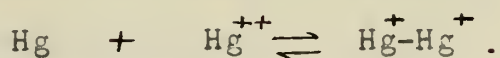
in which P_1 and P_2 are the electrolytic solution pressures of two metals, p_1 and p_2 , the osmotic pressures of the ions and n_1 and n_2 , the valencies of the metals in question. According to his theory, when one metal in mercurial solution, is placed in contact with a solution of a salt of another metal, the above relation must hold in order that the second metal may be precipitated by the first.

A. Ogg (42) applied the conceptions of Nernst and made the first quantitative study of an interaction equilibrium between a

salt solution and an amalgam. In the study of the reactions



and



he discovered that the mercurous ion is di-molecular in aqueous solution.

Then in 1903, L. Kahlenberg took up the study of the rate of the evolution of hydrogen by the action of different metals on aqueous solutions. Previous observations by Baeyer (43), M. D. Tommasi (44) and G. Lemoisne and M. Ditte (45) had suggested that such a study was desirable. G. Fernekes, working under Kahlenberg's direction, (46)(47) investigated the action of sodium and potassium amalgams on various aqueous solutions. He found that solutions of sodium, potassium and barium and certain other chlorides, for example, when acted upon by sodium or potassium amalgam, evolved hydrogen more slowly than pure water. Further he found that the retardation of the rate of the liberation of hydrogen by sodium or potassium amalgam was about the same for isotonic solutions of sodium chloride and potassium chloride. He thought the theory of electrolytic dissociation was out of harmony with these results and referred to it as one of the numerous examples of the "untenability" of the ionic theory" and attempted to explain the facts by a new theory of Kahlenberg's, that of a chemical affinity between solvent and solute, and do away with the conceptions of Arrhenius, which Fernekes said were based upon meager evidence.

G. McP. Smith (48)(49) soon showed that the facts, observed by Fernekes, were entirely in harmony with the theory of electrolytic dissociation and that the ordinary conceptions of ionic theory and mass law were given striking confirmation by all the phenomena observed in the interaction of salt solutions and liquid amalgams.

Since that time, this subject has been studied continuously in this laboratory by G.McP.Smith and in 1910, a quantitative study was offered for the reaction(2)



This was the beginning of a series of investigations under the direction of G.McP.Smith, on the ionic relationships which exist in concentrated aqueous solutions and has led to the development of an entirely independent method for study in the field of solutions of strong electrolytes (3) (4) (5).

III. THEORETICAL.

1.THE REVERSIBLE INTERACTION EQUILIBRIUM.

When a liquid potassium amalgam is placed in contact with a strontium salt in aqueous solution, the potassium, owing to its solution tension, tends to pass into the solution, and there results a difference of potential between the amalgam and the solution. The amalgam becomes negatively charged and attracts the positive ions of the solution, and in case there are no impurities present, strontium ions alone are discharged into the amalgam; this action continues until the solution tension of the strontium in the amalgam has assumed values sufficiently large to prevent the further entrance of strontium from the solution. At this point, equilibrium is established. This reaction has been shown to be reversible, so that if a liquid strontium amalgam containing the same atomic concentration as the above potassium amalgam, is placed in contact with a potassium salt solution of the same normality as the above strontium salt solution, the opposite reaction will take place, with the final establishment of the same equilibri-

um, that is, the two amalgams at equilibrium will show the same ratio of amalgamated metal concentrations and the total concentration of metal equivalents will also be identical with the initial metal equivalent concentration. In other words, two atoms of potassium will enter the solution from the mercury for every atom of strontium discharged into the mercury from the solution, and the reversible reaction may be expressed as



The free energy decrease attending the transfer at the temperature T of that quantity of a substance which is N moles in the state of a perfect gas from an infinite quantity of a solution in which its vapor pressure is p_1 into an infinite quantity of another solution in which its vapor pressure is p_2 is

$$- \Delta F = NRT \log_e \frac{p_1}{p_2} \quad (2)$$

or when in conformity either with Raoult's or with Henry's Law, the vapor pressures are proportional to the mol-fractions

$$- \Delta F = NRT \log_e \frac{x_1}{x_2} \quad (3)$$

The free energy decrease attending the transfer at the temperature T of one atom of strontium from dilute mercurial solution to the ionic state in an aqueous solution is

$$- \Delta F = RT \log_e \frac{F(Sr_{Hg})}{f(Sr^{++})} \quad (4)$$

where $F(Sr_{Hg})$ and $f(Sr^{++})$ are the fugacities of the strontium in mercurial solution and the strontium ion in aqueous solution respectively. The fugacity or "corrected vapor pressure" of Lewis, is a measure of the tendency of a molecular species to escape from a particular thermodynamic environment which surrounds it in solution into that condition of zero thermodynamic environment which prevails in a perfect gas. In the similar transfer of two atoms of potassium, we

have
$$- \Delta F' = 2RT \log_e \frac{F(K_{Hg})}{f(K^+)} = RT \log_e \frac{F(K_{Hg})^2}{f(K^+)^2} \quad (5)$$

At equilibrium, the two attendant free energy decreases are equal and

$$- \Delta F + \Delta F' = 0, \text{ or } RT \log_e \frac{F(Sr_{Hg})}{f(Sr^{++})} = RT \log_e \frac{F(K_{Hg})^2}{f(K^+)^2} \quad (6)$$

whence
$$\frac{F(Sr_{Hg}) (f_{K^+})^2}{F(K_{Hg})^2 (f_{Sr^{++}})} = 1 \quad (7)$$

Of any two metals, either can be made to displace the other from a solution according to the relative magnitudes of

$$\sqrt[n_1]{\frac{F_{Me_1}}{f_{Me_1^+}}} \text{ and } \sqrt[n_2]{\frac{F_{Me_2}}{f_{Me_2^+}}}$$

or the relative magnitudes of the attendant free energy decreases. A reaction always occurs in a direction so as to decrease the free energy content of the system (n_1 and n_2 are the valencies of the two metals in question).

Whether hydrogen will be evolved or not will depend on the relative magnitudes of

$$\frac{F_H}{f_{H^+}} \text{ and } \sqrt[n]{\frac{F_{Me}}{f_{Me^+}}}.$$

When pure materials are used, the reaction between the metals attains equilibrium with such extreme rapidity as compared to that between hydrogen and any one metal that it is possible to study reversible metallic displacements without any added complication due to the evolution of hydrogen.

G. McF. Smith (50) has shown that the solution tension magnitudes of the alkali and alkali earth metals dissolved in dilute mercurial solution decrease in the order

Li, K, Rb, Cs, Na, Ca, Sr, Ba.

However, by the proper manipulation of conditions, one of any pair of the above metals can be made to reversibly displace the other from aqueous solution (24).

The Gibbs-Helmholtz equation has been used to calculate the difference of potential which exists between two amalgams of different concentrations when connected by an electrolyte containing an ion of the metal.

$$E = \frac{RT}{nF} \log_{10} \frac{c_1}{c_2} .$$

Here, E denotes the difference of potential which exists between two amalgams of different concentrations, R the gas constant, T the absolute temperature, n the valence of the ion of the metal, F the value of the Faraday equivalent, and c_1 and c_2 the concentrations of the two amalgams. This equation has been found to hold more accurately the greater the dilution but an increasing deviation was found as the amalgam became more concentrated (51) (52). It has also been shown by J.H. Hildebrand that ideal solution laws may be applied to dilute amalgams (30) (53).

All the present work was carried out with extremely dilute amalgams. The most concentrated equilibrium amalgam contained .0488%K and .0328%Sr.

From the computations of Bates (54) on the partial osmotic pressures of the ions and unionized molecules of KCl and the electromotive force of KCl concentration cells as determined by MacInness and Parker (55), it may be shown that the fugacity of an ion species is approximately proportional to its concentration, as determined by conductivity, even in fairly concentrated solutions and it is the fugacity of the unionized molecules that changes very rapidly with

increasing ion concentration (7) (56).

Assuming that the ratio of the fugacities of two ions in different solutions varies directly as the ratio of the true ionic concentrations, not necessarily those determined by conductivity, and replacing the values of the fugacities of the two metals in the mercurial solution by the concentration fractions of the amalgamated metals, equation 7 becomes

$$\frac{(Sr_{Hg}) (K^+)^2}{(K_{Hg})^2 (Sr^{++})} = Co \quad (8)$$

which is merely the mass law expression for reaction 1.

In the light of the previous discussion upon the mercurial phase

$$Sr_{Hg} = \sum (Sr_{Hg}^0 + SrHg_m)$$

and $K_{Hg} = \sum (K_{Hg}^0 + KHg_n)$, where Sr_{Hg}^0 and K_{Hg}^0 signify the free atoms of the metals dissolved in the mercury.

And

$$Sr^{++} = \sum [Sr(H_2O)_x^{++} + Sr(KCl)_y^{++} + Sr(SrCl_2)_z^{++}, \text{etc.}]$$

$$\text{and } K^+ = \sum [K(H_2O)_{x1}^+ + K(SrCl_2)_{y1}^+ + K(KCl)_{z1}^+, \text{etc.}]$$

that is, the ions, the concentrations of which are measured here, probably include all molecular species, the ionic charge of which is due primarily to the strontium and potassium atoms, regardless of the number or kind of relatively neutral or saturated molecules that may be joined to them by secondary valences.

In equation 8, the amalgamated metal fractions may be obtained by analysis of the equilibrium amalgam but the ionic fractions cannot be ascertained unless the value of Co is known. But at any concentration, c , we may readily obtain the value of the expression

$$\frac{(Sr_{Hg}) (K_{H_2O})^2}{(K_{Hg})^2 (Sr_{H_2O})} = \frac{(Sr_{Hg}) (KSalt)_c^2}{(K_{Hg})^2 (Sr_{Salt})_c} = Cc \quad (9)$$

In any mixed salt solution, the ratio of the salt concentrations must be some function of the ion concentration ratio, i.e.,

$$\frac{(KSalt)_c^2}{(SrSalt)_c} = n \frac{(K^+)_c^2}{(Sr^{++})_c} \quad (10)$$

in which n is some unknown quantity.

If the salt solution is continually made more dilute, n approaches unity as a limit, for at infinite dilution the salts will be completely ionized and the salt concentration ratio will become the ion concentration ratio. As the concentration approaches zero then, the value of C_c will approach that of C_o and an extrapolation of C_c values determined in the case of a fixed salt concentration ratio at several different total salt concentrations to zero total salt concentration should give the value of C_o . The curve obtained was of such a type that a graphical extrapolation would be too inaccurate and so a mathematical method of extrapolation was chosen.

It is also evident that if the exact ion fraction in any salt solution, where C_c could be measured, were known, or in other words if the value of n could be obtained, we could also obtain the value of C_o ; for

$$\frac{(Sr_{Hg}) (KSalt)_c^2}{(K_{Hg})^2 (SrSalt)_c} = \frac{(Sr_{Hg}) (K^+)_c^2 n}{(K_{Hg})^2 (Sr^{++})_c} = C_c = nC_o \quad (11)$$

Assuming conductivity as a measure of ionization at a dilution of .05N and with the use of transference data and the assumption that the Isohydric Principle is valid at this dilution, the value of n may be ascertained and comparisons made as to the ionic fractions obtained in the two cases.

Now in the case of any given equilibrium mixture, it follows from the preceding equations that

$$\frac{(Sr_{Hg})}{(K_{Hg})^2} = Co \frac{(SrSalt)_c}{(KSalt)_c^2} = Co \frac{(Sr^{++})_c}{(K^+)_c^2}$$

That is, in the case of each specific equilibrium mixture, the relationship exists, that

$$\frac{(K^+)^2}{(Sr^{++})} = \frac{Co (KSalt)_c^2}{Cc (SrSalt)_c} = a \quad (12)$$

Expressing the concentrations in terms of mol-fractions, then

$$Sr^{++} + K^+ = 1 \quad \text{and} \quad Sr^{++} = 1 - K^+.$$

We now have two simultaneous equations in which the two unknown quantities are the strontium and potassium ion fractions.

Substituting the value of Sr^{++} in equation 12, we obtain

$$\frac{(K^+)^2}{(1 - K^+)} = a \quad (13)$$

$$\text{whence} \quad K^+ = \frac{-a + \sqrt{a^2 + 4a}}{2} \quad (14)$$

in which a is equal to

$$\frac{Co (KSalt)_c^2}{Cc (SrSalt)_c}.$$

Therefore, after having determined the value of Co , it is possible to determine the ion fractions of the metals in solutions containing the salts at a fixed mol-fraction ratio.

In mixtures, in which the salts are present in different mol-fraction ratios, two and four equivalents of each salt to the other were studied, the most dilute total salt concentration which could be studied was .20N. However, the same value of the mass law expression, Co , must obtain regardless of the ratio of the ~~total~~ salt concentration fractions as long as the total concentration of metals in the mercurial phase is kept constant. In all calculations of ion fractions in this paper in solutions at 25°C, the value of Co for a

concentration of .20 milli-equivalents of metals per ten grams of mercury was used.

2. THE MERCURIAL PHASE AND THE MASS LAW.

A metal in dilute mercurial solution exerts a solution tension or tendency to pass into the ionic condition when the amalgam is brought in contact with an aqueous salt solution. This tendency is some function of the inherent property of the metal itself and the mercurial environment in which it is placed. In the sense of the reaction



a certain concentration of metal hydrargyride yields a definite concentration of free metal atoms and consequently a definite solution tension.

In the case of the study of the potassium-sodium equilibrium with the use of solutions of fixed salt ratio and fixed total concentration, G. McP. Smith and T. R. Pall found that changes in the amalgam concentration lead to changes in the value of the equilibrium expression, C_c , between the amalgamated metal fractions in the equilibrium amalgam and the salt fractions in the aqueous solution. G. McP. Smith and S. A. Braley found that this was even more marked in the case of the strontium-sodium equilibrium. And now in this study the same fact was observed. This can only be interpreted in the light of the above equation; different concentrations of hydrargyrides produce different free metal atom concentrations and consequently different values for the expression, C_c .

The mass law expression for the reaction in a liquid amalgam is

$$\frac{(\text{Me}) (\text{Hg})^x}{(\text{MeHg}_x)} = K_m$$

But, since the solvent in which the equilibrium exists is mercury and the amalgams are all extremely dilute, the mol-fraction of the mer-

cury may be taken as unity and

$$\frac{(Me)}{(MeHg_x)} = K_m \quad \text{or} \quad \frac{\alpha}{1 - \alpha} = K_m$$

where α is the degree of dissociation of the hydrargyride. Then

$$\alpha = \frac{K_m}{1 + K_m} = \text{const.}$$

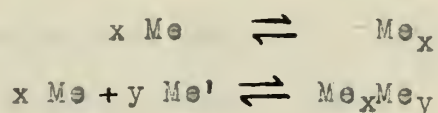
In other words, if the same mass law holds in the sense of the above equation, the degree of dissociation of the hydrargyride remains constant and the free metal atom concentration is directly proportional to the hydrargyride concentration; i.e., the solution tension is a linear function of the hydrargyride concentration. The manifestation of the magnitude of the solution tension is the value of the equilibrium expression, C_c , and we can write

$$(MeHg_x) = kP_{Me} = k'C_c \quad \text{where } P_{Me} \text{ is}$$

the solution tension of the initial amalgam. As a necessary consequence, then, of the mass law in the sense of the reaction in the liquid amalgam, C_c should be a linear function of the amalgam concentration. Conversely, if C_c is found to be a linear function of amalgam concentration we shall say that the mass action expression

$$\frac{(Me)(Hg)^x}{(MeHg_x)} = K_m$$

is valid for those concentrations of mercurial solutions. However, the existence of other equilibria in the mercurial solution, such as



and $MeHg_x + Me'Hg_y \rightleftharpoons MeMe'Hg_{(x+y)}$, etc.

which might occur in such a manner so as to introduce compensating errors and affect the mass action constant, K_m , by a constant factor, is not at all precluded.

3. THE AMALGAM AT EQUILIBRIUM.

When any amalgam has been brought into equilibrium with a particular salt solution, it has been forced to adapt its metal concentrations so that the solution tension of each metal is zero with respect to the particular ion with which it is in equilibrium.

Therefore, as has been shown by Nernst, at equilibrium

$$\frac{(Sr_{Hg}^0)}{(Sr^{++})} = \frac{(K_{Hg}^0)^2}{(K^+)^2}$$

and the equilibrium constant between the atoms in the mercurial solution and the ions in the aqueous solution, is unity.

$$\frac{(Sr_{Hg}^0)(K^+)^2}{(Sr^{++})(K_{Hg}^0)^2} = 1.$$

It must necessarily follow that

$$(Sr_{Hg}^0) = (Sr^{++}) \quad \text{and} \quad (K_{Hg}^0) = (K^+)$$

or the free atom fractions in the mercurial phase are identical in value to the ionic fractions in the aqueous phase for each respective metal at equilibrium.

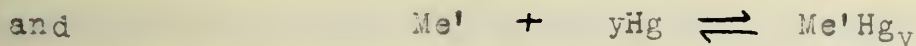
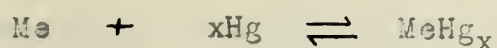
Since, upon analysis of the equilibrium amalgam, the fraction of each amalgamated metal may be determined and also the total number of amalgamated metal atoms, that is $\sum(Me_{Hg}^0 + MeHg_x)$, it is possible to determine the total number of strontium and potassium atoms, free and combined, at equilibrium. If the total number of strontium atoms is N_{Sr} and the total number of potassium atoms is N_K and β and α are the respective degrees of dissociation of the metal hydrargyrides into free metal atoms, then

$$\frac{\alpha N_K}{\alpha N_K + \beta N_{Sr}} = K^+.$$

It has been shown how the potassium ion fraction may be obtained and

so if $\alpha = 1$, we can solve for β and obtain the relative degrees of dissociation of the strontium hydrargyride as compared to the potassium hydrargyride at any amalgam concentration when in equilibrium with a particular solution.

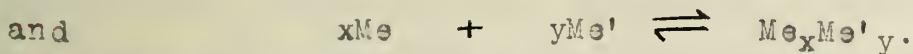
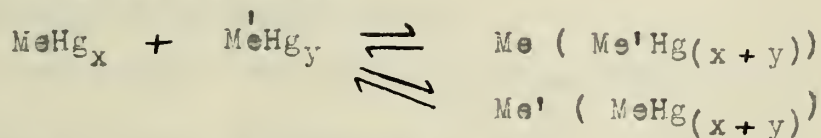
It has also been shown that $\alpha = \text{const.}$ for a hydrargyride at any concentration and similarly $\beta = \text{const.}$ for some other hydrargyride at any concentration. Now if the mass law is applicable to each of the two equilibria in the presence of the other



it must necessarily follow that

$$\frac{\alpha}{\beta} = \text{const.} \quad \text{for every equilibrium amalgam.}$$

If this ratio is not constant for the different equilibrium amalgams, then other equilibria must exist in the amalgams where two hydrargyrides co-exist, such as



A study of the different equilibrium amalgams will afford interesting evidence of the existence of such equilibria.

IV. MATERIALS, APPARATUS, AND METHOD OF EXPERIMENTATION.

1. MATERIALS. In order to prevent the occurrence of the side reaction of the liberation of hydrogen, which is catalyzed with extreme ease by traces of heavy metals such as iron or aluminum (57) (58), it was necessary to use only the purest of materials.

(a). Water. The distilled water of the laboratory was successively distilled from alkaline potassium permanganate and dilute sulphuric acid as described in the preceding papers of this series.

(b). Potassium Chloride. A good grade of commercial salt was recrystallized twice from distilled water. Each time the mother liquor was removed as completely as possible by filtration at the suction pump and then the remainder was thrown off in a high speed electrical centrifuge. The salt was dried in an electric oven at 150°C , but finally before use it was heated in the electric muffle for two hours at a temperature not exceeding dull redness and then cooled in a desiccator containing calcium-chloride.

(c) Strontium Chloride. The commercial salt was first recrystallized from distilled water containing a little hydrochloric acid and finally from pure water. The mother liquor was removed after each crystallization as before and finally the salt was dried for several days over calcium-chloride. The salts were all examined spectroscopically before use.

(d). Ammonium Carbonate. That of Eimer and Amend, Tested Purity, was used. Upon ignition of five grams in a Platinum dish, no residue was obtained.

(e). Hydrochloric Acid. Gaseous hydrogen chloride was prepared by treating commercial NaCl with concentrated H_2SO_4 and passed into distilled water. The K_2SO_4 residue obtained in the analysis of the

equilibrium amalgams was invariably colored a decided pink with Fe_2O_3 when the ordinary HCl of the laboratory was used.

(f). Mercury. Commercial mercury was filtered through a pin-hole filter, shaken in a heavy separatory funnel with a dilute solution of sulphuric acid and potassium dichromate (59), washed, passed through a column of mercurous-nitrate in dilute nitric acid, again washed, dried, and finally distilled from a 200 c.c. Claisen bulb in a slow current of air. It was again run through the nitric acid-mercurous nitrate column to remove the little oxide of mercury before use.

(g). The amalgams were prepared by the electrolysis of saturated salt solutions with mercury cathodes as described by G.McP.Smith and H.C.Bennett (58). They were usually made fairly concentrated, then analyzed and diluted with mercury to the desired strength before using.

2. APPARATUS. A description of the apparatus used in this investigation will be found in the paper by G.McP.Smith and T.R.Ball (4).

3. METHOD OF EXPERIMENTATION.

(a). Solutions. Separate solutions of KCl and SrCl_2 were made up, each equal in concentration to the total concentration desired for the mixed salt solution. Then by mixing these solutions in the proper volume relations in "Resistenz" glass bottles, it was possible to prepare solutions of the particular total concentration and salt concentration ratio desired.

The pure dry KCl was weighed out in calculated quantities, dissolved in pure water, transferred to calibrated volumetric flasks, and diluted to the mark at 25°C .

The SrCl_2 was weighed out in sufficient quantity to give a solution slightly more concentrated than that desired. After determining the normality by the Volhard volumetric method for chlorine, the strontium salt solutions were accurately diluted to the normality desired (60). After diluting and mixing the two solutions in the desired ratio, the normality of the resulting solution was generally checked by the Volhard method.

(b). Equilibrium. As it was desired in each run to start with amalgams having as nearly as possible the same equivalent concentration, the analyzed stock amalgams were diluted with mercury to the concentration decided upon. The mercury for dilution was weighed out on a small trip balance with an accuracy of .1-.2 grams, and then placed in the reaction flask. Fifty cubic centimeters of the mixed salt solution were next added, and the whole balanced on the trip balance. A sufficient quantity of the stock amalgam was then added to give the desired concentration. The flask containing the reaction mixture was at once placed in the thermostat, and shaken for fifteen minutes, after which the solution was decanted from the amalgam; a fresh portion of the solution was immediately added, the flask again placed in the thermostat, shaken for fifteen minutes and the solution again decanted. When extremely dilute solutions were used, the amalgams were treated in this manner with ten successive portions of the solution; usually only six renewals were required, while in the case of the more concentrated solutions not so many were necessary to produce the desired equilibrium. After decanting the last portion of the solution, the amalgams were washed and decomposed with HCl . Each run was made with six separate reaction mixtures, three of which were started with potassium amalgam and three with strontium amalgam.

(c). Treatment of the Decomposition Products. The HCl solution containing the potassium and strontium from the equilibrium amalgam was in each case quantitatively withdrawn from the mercury in the decomposition flask, evaporated to dryness in platinum dishes on the steam bath and then analyzed for strontium and potassium. The mercury itself was dried and accurately weighed to 0.1-0.2 grams.

(d). Determination of Potassium and Strontium. The mixed chloride residue was dissolved in about 50 c.c. of water, dilute H_2SO_4 was added in slight excess, and then a quantity of alcohol equal to the volume of the solution. This solution was allowed to stand, usually over night, and then it was filtered through an asbestos-matted Gooch crucible, washed thoroughly with 50% alcohol containing a small quantity of H_2SO_4 and finally with pure alcohol. The crucible containing the SrSO_4 was then dried in the electric oven and finally ignited inside a larger crucible provided with an asbestos ring so as to maintain an air bath around the precipitate during the ignition.

The filtrate from the SrSO_4 was evaporated to a small volume, transferred to a weighed platinum dish and evaporated to dryness. The final residue was then ignited at a temperature not exceeding dull redness, after ammonium carbonate had been lightly scattered over the surface to aid the decomposition of any $\text{K}_2\text{S}_2\text{O}_7$ to K_2SO_4 (60).

V. EXPERIMENTAL DATA.

The data obtained in this investigation is recorded in the following tables. Unless otherwise stated, the figures in the first column in each table refer to the number of the experiment; the second column indicates the amalgam used at the start; the third, fourth and fifth columns contain the quantities in grams obtained in the analysis of the equilibrium amalgam; column six shows the concentration of the amalgam, at equilibrium, in total milli-equivalents of amalgamated metals per ten grams of mercury, as calculated from the analytical data; columns seven and eight give the amalgamated metal fractions in the equilibrium amalgam, as calculated from columns three and four; column nine contains the value of the expression

$$\frac{(Sr_{Hg}) (K_{Salt})^2}{(K_{Hg})^2 (Sr_{Salt})c} = Cc$$

in which (Sr_{Hg}) and (K_{Hg}) are the amalgamated metal fractions from columns seven and eight and (K_{Salt}) and (Sr_{Salt}) are the respective mol-fractions of salts in the aqueous solution. This equilibrium expression was expressed in this manner, rather than in equivalent fractions, because the values of Cc thus obtained were found to be a linear function of the amalgam concentration, expressed in milli-equivalents per ten grams of mercury; this fact greatly simplified the study. Column ten contains the values of Cc corrected to some specific amalgam concentration. The individual values in each set of experiments were corrected in all cases to the average amalgam concentration of the experiments in that set by a simple proportion.

1. EFFECT OF VARYING THE CONCENTRATION OF THE LIQUID AMALGAM AT VARIOUS TOTAL SALT CONCENTRATIONS, BUT AT A FIXED (EQUIVALENT) SALT-CONCENTRATION RATIO. In the case of the sodium-potassium

equilibrium and also in the sodium-strontium equilibrium, it has previously been observed that changing the concentration of the liquid amalgam exerts a decided effect upon the value of the equilibrium expression, C_c . Smith and Braley found that C_c was a linear function of amalgam concentration for solutions of any specific total salt concentration, as long as the salts were present in equivalent proportions. Similar results were obtained in this investigation in which solutions of a total concentration of 0.10N, 0.20N, 0.40N, 0.80N, 1.60N and 3.00N were studied, containing equivalent proportions of salts. Data obtained will be found in Tables II, III, IV, V, VI and VII. Table I shows the data for 0.05N; here, only one set of experiments was made and since C_c was found to be a linear function of amalgam concentration for all other salt concentrations, it was assumed to be so here.

The values of C_c were plotted as ordinates against the total amalgam concentration in milli-equivalents per 10 grams of mercury, as abscissas, as shown in Fig. I. Each point indicated in the plot is the average of a set of corrected C_c values, each set usually containing from six to twelve experiments. In Tables III and IV it will be noted that, with the most concentrated amalgams, the values of C_c are not quite concordant and also in Fig. I that, when plotted, the average of these experiments do not fall upon the line obtained with the more dilute amalgams. Similar disagreement in data was also found in the sodium-potassium study by Smith and Ball and also in the sodium-strontium study by Smith and Braley when highly concentrated amalgams were used.

In any one set of experiments, the concentration of the equilibrium amalgam always differed somewhat in the different individual experiments, because the amalgam was weighed out more or less roughly

on a trip balance, and also because the evolution of hydrogen, which always occurred to a small extent, varied in the individual experiments.

2. EFFECT OF VARYING THE TOTAL SALT CONCENTRATION AT VARIOUS AMALGAM CONCENTRATIONS BUT AT A FIXED (EQUIVALENT) SALT CONCENTRATION RATIO.

Table VIII contains the data which show the effect of increasing the total salt concentration in stages from 0.05N to 3.00N at several amalgam concentrations, the salts in all cases being present in equivalent proportions. The different values of C_c were obtained by simply reading them from the plots in Fig. 1 at the desired amalgam concentration. The values in parenthesis were obtained by extrapolation of the lines out from the region covered by experimental data. Fig. 2 shows the value of C_c as a function of the total salt concentration at different specific amalgam concentrations.

In the previous studies by means of this distribution method, the most dilute solution studied was 0.20N. As pointed out in the theoretical discussion, an extrapolation of the curve shown in Fig. 2 to infinite dilution (where the salts are entirely ionized and the salt-concentration ratio then becomes the ion concentration ratio) should give the desired value of C_o , the equilibrium constant between the ions in the water and the metals in the mercury. In order to make this extrapolation to zero concentration as certain as possible, attempts were made to study solutions more dilute than 0.20N. It was found possible to study solutions of a total concentration of both 0.10N and 0.05N; the data are shown in Tables I and II. But even now a graphical extrapolation of the curve, of the type obtained as shown in Fig. 2, must be regarded as extremely inaccurate; and therefore it was decided to obtain the value of C_o by a mathematical extrapolation.

TABLE I.

MIXED AQUEOUS PHASE 0.05N

KCl : $1/2 \text{ SrCl}_2$.

TEMPERATURE 25°C.

No.	Amal. at Start.	Analysis of the Equilibrium Amalgam.			Milli-equivs. of Metals per 10 g.Hg	Amalgamated Metal Fractions		Cc	Cc corr.to .0684 mg.equiv.
		K ₂ SO ₄	SrSO ₄	Hg		K	Sr		
1	Sr	.0469	.2021	391.9	.0700	.3291	.6709	8.25	8.07
2	Sr	.0494	.2166	387.6	.0755	.3252	.6748	8.50	7.70
3	Sr	.0499	.2319	396.4	.0782	.3122	.6878	9.39	8.22
4	K	.0461	.1919	406.3	.0644	.3364	.6636	7.81	8.29
5	K	.0499	.2059	408.9	.0688	.3381	.6619	7.71	7.67
6	K	.0474	.1954	395.8	.0676	.3386	.6614	7.68	7.77
7	Sr	.0476	.1951	400.4	.0667	.3402	.6598	7.59	7.78
8	Sr	.0517	.2331	410.5	.0708	.3393	.6607	7.65	7.39
9	Sr	.0508	.2343	403.0	.0768	.3138	.6862	9.28	8.26
10	K	.0450	.1862	397.1	.0641	.3376	.6624	7.74	8.26
11	K	.0440	.1634	402.8	.0567	.3628	.6372	6.45	7.78
12	K	.0460	.1803	406.0	.0614	.3494	.6506	7.10	7.92
Mean					.0684				7.93

TABLE II.

MIXED AQUEOUS PHASE 0.10N

corr.to
.1401

1	Sr	.0566	.2364	205.1	.1571	.3355	.6645	7.86	7.02
2	Sr	.0555	.2247	204.8	.1506	.3423	.6577	7.48	6.96
3	Sr	.0536	.2140	201.3	.1464	.3459	.6541	7.28	6.97
4	K	.0469	.1622	192.1	.1200	.3792	.6208	5.75	6.72
5	K	.0493	.1843	200.0	.1285	.3603	.6397	6.56	7.16
6	K	.0533	.2044	205.1	.1383	.3545	.6455	6.84	6.92
Mean					.1401				6.96
									corr.to .0743
7	Sr	.0704	.1753	399.4	.0680	.4585	.5415	3.42	3.74
8	Sr	.0793	.2188	402.8	.0817	.4334	.5666	4.02	3.67
9	Sr	.0801	.2377	407.8	.0860	.4156	.5844	4.50	3.89
10	K	.0724	.1788	405.7	.0685	.4605	.5395	3.39	3.68
11	K	.0697	.1800	405.6	.0680	.4497	.5503	3.62	3.96
12	K	.0730	.2002	410.0	.0737	.4349	.5651	3.98	4.01
Mean					.0743				3.83

TABLE 111

MIXED AQUEOUS PHASE 0.20N

KCl : $1/2$ SrCl₂.

TEMPERATURE 25° C.

No.	Amal. at Start.	Analysis of the Equilibrium Amalgam			Milli-equivs. of Metals per 10 g. Hg	Amalgamated Metal Fractions		Cc mg.	Cc corr.to .6138 equiv.
		K ₂ SO ₄	SrSO ₄	Hg		K	Sr		
1	Sr	.0752	.4886	98.7	.6265	.2453	.7547	16.7	16.3
2	Sr	.0738	.4585	98.5	.5928	.2532	.7468	15.5	16.0
3	Sr	.0749	.4612	98.2	.5987	.2551	.7449	15.2	15.6
4	K	.0691	.4733	96.3	.6174	.2353	.7647	18.4	18.3
5	K	.0758	.5069	102.8	.6213	.2396	.7604	17.7	17.4
6	K	.0734	.4999	100.4	.6259	.2362	.7638	18.2	17.9
Mean					.6138				16.9
									corr.to .3111
7	Sr	.0591	.2480	102.3	.3303	.3342	.6658	7.94	7.48
8	Sr	.0667	.3049	108.7	.3758	.3154	.6846	9.17	7.59
9	Sr	.0613	.2590	103.2	.3414	.3328	.6672	8.02	7.30
10	K	.0514	.1860	103.6	.2525	.3685	.6315	6.19	7.62
11	K	.0586	.2206	106.8	.2879	.3591	.6409	6.62	7.17
12	K	.0555	.2113	105.4	.2788	.3562	.6438	6.77	7.55
Mean					.3111				7.45
									corr.to .1805
13	Sr	.0894	.2615	202.3	.1914	.4188	.5812	4.41	4.16
14	Sr	.0868	.2505	203.9	.1827	.4223	.5777	4.32	4.27
15	Sr	.0952	.2935	207.1	.2070	.4059	.5941	4.81	4.18
16	K	.0855	.2334	209.1	.1685	.4360	.5640	3.95	4.23
17	K	.0893	.2511	209.0	.1800	.4285	.5715	4.15	4.17
18	K	.0804	.2031	204.2	.1535	.4549	.5451	3.51	4.13
Mean					.1805				4.19
									corr.to .1511
19	Sr	.0741	.1754	192.6	.1433	.4716	.5284	3.17	3.34
20	K	.0737	.1875	192.0	.1504	.4534	.5466	3.54	3.55
21	K	.0864	.2214	213.2	.1596	.4515	.5485	3.58	3.39
Mean					.1511				3.43
									corr.to .0676
22	Sr	.0999	.1779	396.0	.0778	.5440	.4560	2.05	1.78
23	Sr	.1061	.1914	398.3	.0829	.5408	.4592	2.09	1.70
24	K	.0921	.1243	382.6	.0630	.6093	.3907	1.40	1.51
25	K	.0910	.1231	388.4	.0614	.6095	.3905	1.40	1.54
26	K	.0795	.1069	400.2	.0526	.6107	.3893	1.39	1.79
Mean					.0676				1.66

TABLE IV

MIXED AQUEOUS PHASE 0.40N

KCl : 1/2 SrCl₂

TEMPERATURE 25° C.

No.	Amal. at Start.	Analysis of the Equilibrium Amalgam.			Milli-equivs. of Metals per 10 g. Hg	Amalgamated Metal Fractions.		Cc	Cc corr.to .6339 mg.equiv.
		K ₂ SO ₄	SrSO ₄	Hg		K	Sr		
1	Sr	.0577	.2731	53.0	.6859	.3083	.6917	9.68	8.93
2	Sr	.0646	.2620	67.0	.5363	.3422	.6578	7.49	8.84
3	Sr	.0565	.2685	53.6	.6664	.3077	.6923	9.73	9.50
4	K	.0538	.2473	52.3	.6330	.3150	.6850	9.20	9.22
5	K	.0520	.2352	49.0	.6444	.3175	.6825	9.02	8.87
6	K	.0581	.2595	54.8	.6376	.3208	.6792	8.79	8.72
Mean					.6339				9.01
									corr.to .5327
7	Sr	.0871	.3147	99.5	.4449	.3685	.6315	6.19	7.42
8	Sr	.0933	.4169	99.0	.5667	.3208	.6792	8.78	8.23
9	K	.0957	.3972	98.4	.5511	.3372	.6628	7.77	7.51
10	K	.0985	.3848	99.3	.5357	.3505	.6495	7.05	7.02
11	K	.0979	.4211	101.0	.5651	.3288	.6712	8.27	7.78
Mean					.5327				7.59
									corr.to .3176
12	Sr	.0677	.1714	99.5	.2655	.4547	.5453	3.51	4.19
13	Sr	.0793	.2305	100.8	.3392	.4205	.5795	4.36	4.08
14	Sr	.0696	.1807	104.8	.2639	.4478	.5522	3.67	4.42
15	Sr	.0754	.2119	98.0	.3237	.4283	.5717	4.16	4.08
16	K	.0779	.2247	100.3	.3332	.4225	.5775	4.31	4.11
17	K	.0649	.1856	81.8	.3339	.4242	.5758	4.26	4.05
18	K	.0948	.2931	107.8	.3972	.4057	.5943	4.81	3.85
19	K	.0711	.1856	99.8	.2843	.4468	.5532	3.69	4.12
Mean					.3176				4.11
									corr.to .1730
20	Sr	.1252	.2632	197.7	.2176	.5008	.4992	2.65	2.11
21	Sr	.1179	.2229	204.0	.1852	.5272	.4728	2.23	2.11
22	Sr	.1153	.2135	204.4	.1785	.5327	.4673	2.20	2.13
23	K	.0940	.1567	201.1	.1384	.5586	.4414	1.88	2.35
24	K	.0997	.1675	204.5	.1455	.5568	.4432	1.90	2.26
Mean					.1730				2.19
									corr.to .0881
25	Sr	.1440	.1851	394.0	.0931	.6211	.3789	1.31	1.24
26	Sr	.1700	.2410	417.2	.1097	.5980	.4020	1.49	1.20
27	Sr	.1519	.1832	398.9	.0937	.6361	.3639	1.20	1.13
28	K	.1251	.1363	399.0	.0732	.6595	.3405	1.04	1.25
29	K	.1285	.1478	393.8	.0784	.6471	.3529	1.12	1.26
30	K	.1340	.1523	398.4	.0803	.6501	.3499	1.10	1.21
Mean					.0881				1.22

TABLE V

MIXED AQUEOUS PHASE 0.80N

KCl : 1/2 SrCl₂

TEMPERATURE 25° C.

No.	Amal. at Start	Analysis of the Equilibrium Amalgam			Milli-equivs. of Metals per 10 g. Hg	Amalgamated Metal Fractions		Cc	Cc corr.to .6779 mg.equiv
		K ₂ SO ₄	SrSO ₄	Hg		K	Sr		
1	Sr	.1420	.4361	99.4	.6416	.4063	.5937	4.79	5.07
2	Sr	.1474	.4834	97.3	.7149	.3916	.6084	5.28	5.01
3	Sr	.1477	.4954	101.0	.7020	.3859	.6141	5.49	5.30
4	K	.1423	.5145	101.0	.7165	.3685	.6315	6.18	5.85
5	K	.1407	.4328	101.5	.6235	.4069	.5931	4.77	5.19
6	K	.1415	.4620	99.5	.6687	.3924	.6076	5.26	5.33
Mean					.6779				5.35
									corr.to .3240
7	Sr	.1086	.2449	104.5	.3746	.4835	.5165	2.94	2.54
8	Sr	.1037	.2345	102.0	.3670	.4829	.5171	2.96	2.61
9	K	.0868	.1697	99.6	.2856	.5192	.4808	2.37	2.69
10	K	.1058	.2159	101.6	.3509	.5082	.4918	2.54	2.35
11	K	.0810	.1395	101.3	.2418	.5508	.4492	1.97	2.65
Mean					.3240				2.57
									corr.to .1678
12	Sr	.1255	.1586	199.1	.1590	.6252	.3748	1.28	1.35
13	Sr	.1326	.1647	205.1	.1617	.6291	.3709	1.25	1.30
14	K	.1341	.1895	200.2	.1800	.5988	.4012	1.49	1.39
15	K	.1479	.1865	212.7	.1752	.6259	.3741	1.27	1.22
16	K	.1455	.1762	220.0	.1631	.6352	.3648	1.20	1.23
Mean					.1678				1.30

TABLE VI

MIXED AQUEOUS PHASE 1.60N

KCl : 1/2 SrCl₂.

TEMPERATURE 25°C.

No.	Amal. at Start.	Analysis of the Equilibrium Amalgam			Milli-equivs. of Metals per 10 g. Hg.	Amalgamated Metal Fractions		Cc	Cc corr.to .1729 mg.equiv
		K ₂ SO ₄	SrSO ₄	Hg		K	Sr		
1	Sr	.1360	.1512	198.0	.1620	.6551	.3449	1.07	1.14
2	Sr	.1487	.1656	199.6	.1760	.6545	.3455	1.07	1.05
3	Sr	.1498	.1846	198.8	.1876	.6312	.3688	1.23	1.13
4	K	.1468	.1866	201.4	.1845	.6240	.3760	1.29	1.21
5	K	.1355	.1409	200.2	.1542	.6696	.3304	0.98	1.10
Mean					.1729				1.13
									corr.to .0825
6	Sr	.1576	.1405	400.2	.0834	.7031	.2969	0.80	0.79
7	Sr	.1710	.1418	412.6	.0850	.7179	.2821	0.73	0.71
8	Sr	.1821	.1567	403.2	.0942	.7104	.2896	0.76	0.67
9	K	.1568	.1301	395.4	.0813	.7178	.2822	0.73	0.74
10	K	.1528	.1307	398.8	.0795	.7116	.2884	0.76	0.79
11	K	.1401	.1147	397.1	.0719	.7204	.2796	0.72	0.82
Mean					.0825				0.75

TABLE VII

MIXED AQUEOUS PHASE 3.00N

corr.to
.3505

1	Sr	.1268	.2158	106.6	.3569	.5534	.4466	1.94	1.91
2	Sr	.1068	.2150	103.4	.3448	.5115	.4885	2.48	2.52
3	Sr	.1229	.2471	101.7	.4032	.5122	.4878	2.48	2.16
4	K	.1090	.2034	105.4	.3287	.5304	.4696	2.22	2.36
5	K	.1004	.2207	103.7	.3430	.4897	.5103	2.83	2.89
6	K	.1056	.1943	102.0	.3264	.5339	.4661	2.18	2.34
Mean					.3505				2.36

FIG. 1

SHOWING VALUE OF C_C AS A FUNCTION
OF AMALGAM CONCENTRATION AT
DIFFERENT TOTAL SALT CONCENTRATIONS.

EQUIVALENT PROPORTIONS OF
K AND SR IN AQUEOUS PHASE.
TEMP. 25°C

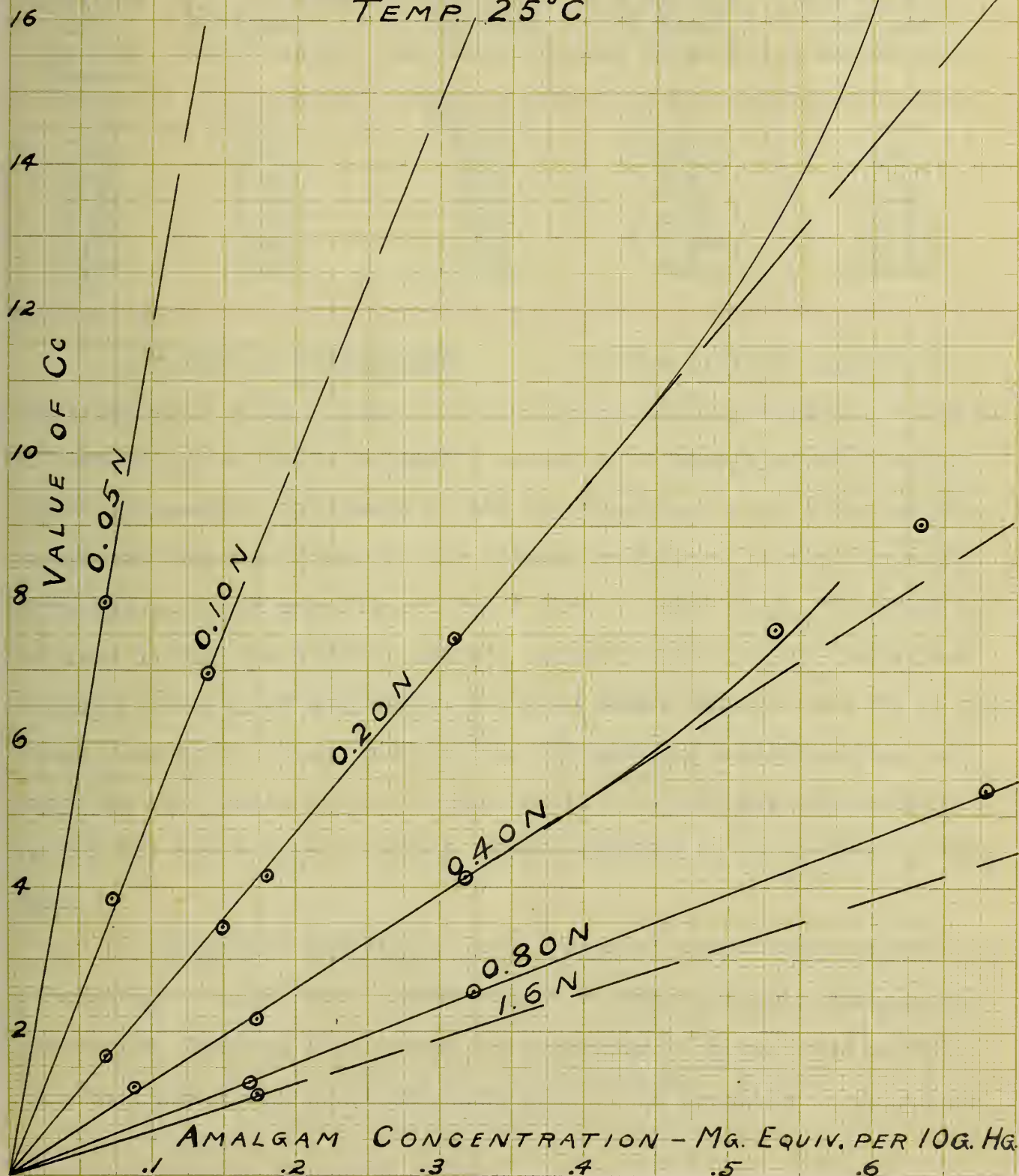


TABLE VIII

SHOWING THE VALUE OF C_c AS A FUNCTION OF TOTAL SALT CONCENTRATION AT A FIXED (EQUIVALENT) SALT CONCENTRATION RATIO AND AT VARIOUS SPECIFIC AMALGAM CONCENTRATIONS AT 25° C.

Normality Of Aqueous Phase	0.1 mg.equiv. of metal per 10 g. Hg	0.2 mg.equiv. of metal per 10 g. Hg	0.3 mg.equiv. of metal per 10 g. Hg	0.4 mg.equiv. of metal per 10 g. Hg
0.05	11.70	(23.40)		
0.10	5.05	9.95	(14.90)	
0.20	2.40	4.75	7.15	9.55
0.40	1.30	2.60	3.90	5.20
0.80	0.78	1.55	2.35	3.15
1.60	0.62	1.28	(1.90)	(2.55)
3.00	0.65	1.35	2.05	(2.70)

3. EFFECT OF TEMPERATURE.

All the previous experiments outlined were carried out at 25°C. Similar studies were also made at a temperature of 40°C, primarily to see if a change of 15°C would cause any marked difference in the ion fractions of the two metals, potassium and strontium, in the aqueous solution. It will be seen from Tables X, XI and XII and Fig.3 that at 40°C also, the value of C_c is a linear function of amalgam concentration for the solutions studied, 0.20N, 0.40N and 0.80N. Table IX shows data for 0.10N; in this case, experiments were made at only one amalgam concentration, but since C_c was found to be a linear function of amalgam concentration in all the other cases studied, it was assumed to be so also in this case.

In Table XIII and Fig.4, data are given which show that C_c , as a function of total salt concentration at some specific amalgam concentration, behaves in a manner very similar to that found at 25°C. From the data obtained at 25°C and 40°C it is possible to calculate

FIG. 2

SHOWING VALUE OF CC AS A FUNCTION
OF TOTAL SALT CONCENTRATION
AT VARIOUS AMALGAM CONCENTRATIONS.

EQUIVALENT PROPORTIONS OF K
AND SR IN AQUEOUS PHASE.
TEMP. $25^{\circ}C$

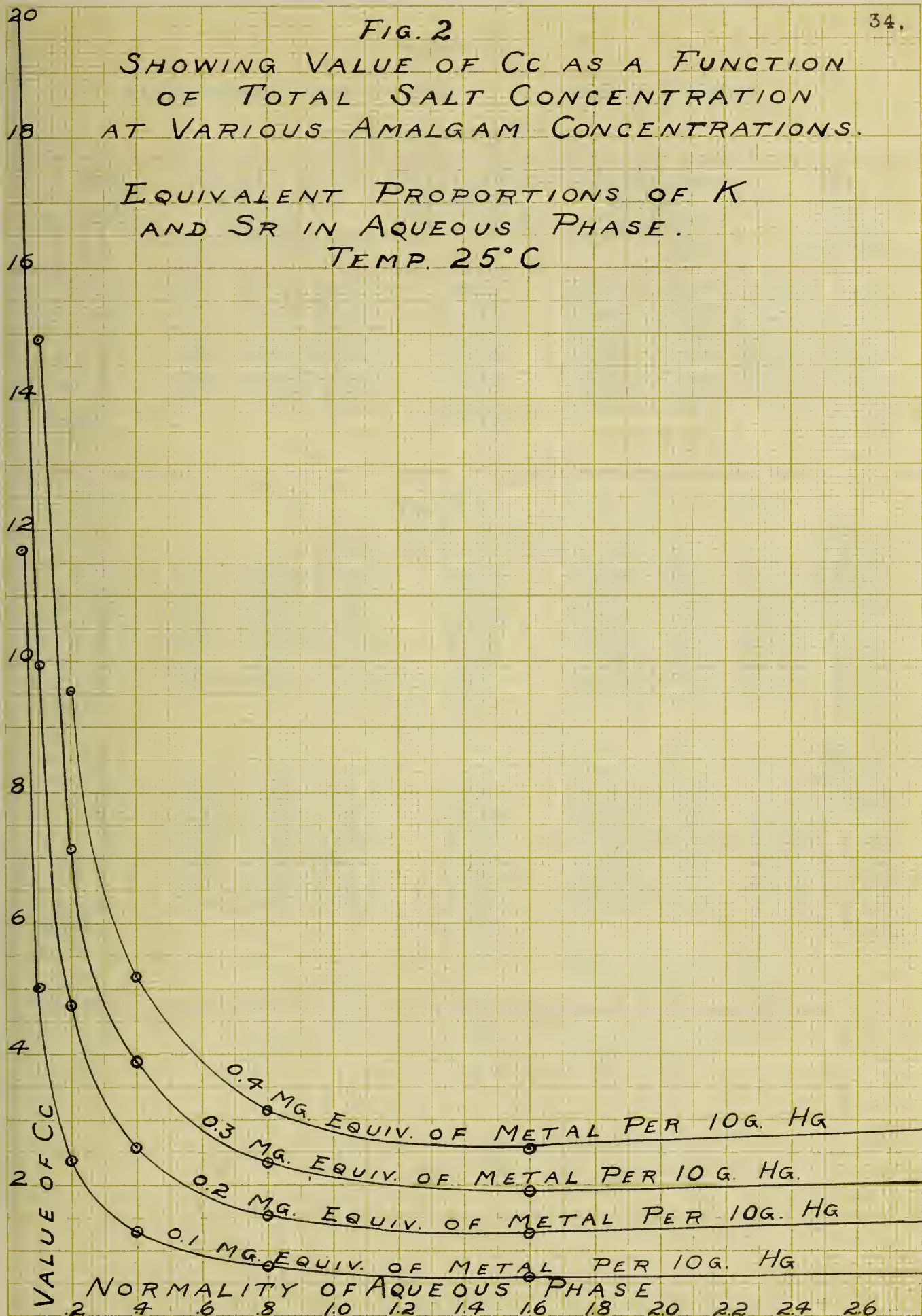


TABLE 1X.

MIXED AQUEOUS PHASE 0.10N

KCl : 1/2 SrCl₂

TEMPERATURE 40°C.

No.	Amal. at Start.	Analysis of the Equilibrium Amalgam			Milli-equivs. of Metals per 10 g.Hg	Amalgamated Metal Fractions		Cc	Cc corr.to .0814 mg.equiv.
		K ₂ SO ₄	SrSO ₄	Hg		K	Sr		
1	Sr	.0491	.2442	406.7	.0792	.2973	.7027	10.59	10.90
2	Sr	.0478	.2427	400.1	.0797	.2940	.7060	10.88	11.10
3	Sr	.0534	.2830	407.7	.0907	.2848	.7152	11.75	10.52
4	K	.0480	.2376	399.7	.0785	.2993	.7007	10.42	10.82
5	K	.0468	.2446	400.9	.0798	.2875	.7125	11.48	11.70
6	K	.0482	.2438	406.5	.0803	.2896	.7104	11.28	11.42
Mean					.0814				11.08

TABLE X

MIXED AQUEOUS PHASE 0.20N

corr.to
.3514

1	Sr	.0372	.2556	99.9	.3214	.2349	.7651	18.47	20.20
2	Sr	.0410	.2931	107.9	.3394	.2277	.7723	19.83	20.50
3	Sr	.0410	.2881	104.3	.3459	.2308	.7692	19.24	19.60
4	K	.0429	.3149	109.1	.3596	.2235	.7765	20.70	20.30
5	K	.0401	.3088	102.5	.3730	.2149	.7851	22.64	21.30
6	K	.0407	.3017	102.0	.3680	.2217	.7783	21.09	20.15
Mean					.3514				20.34

corr.to
.1642

7	Sr	.0552	.2551	191.8	.1780	.3134	.6866	9.31	8.58
8	Sr	.0532	.2404	198.9	.1624	.3183	.6817	8.96	9.05
9	Sr	.0536	.2445	184.8	.1774	.3165	.6835	9.08	8.42
10	K	.0527	.2435	201.1	.1619	.3139	.6861	9.27	9.41
11	K	.0523	.2314	204.7	.1525	.3229	.6771	8.64	9.30
12	K	.0544	.2238	199.9	.1531	.3388	.6612	7.67	8.26
Mean					.1642				8.84

TABLE XI

MIXED AQUEOUS PHASE 0.40N

KCl : 1/2 SrCl₂

TEMPERATURE 40°C.

No.	Amal. at Start.	Analysis of the Equilibrium Amalgam			Milli-equivs. of Metals per 10 g. Hg	Amalgamated Metal Fractions		Cc	Cc corr.to .3444 mg.equiv.
		K ₂ SO ₄	SrSO ₄	Hg		K	Sr		
1	Sr	.0590	.2530	106.0	.3239	.3297	.6703	8.22	8.75
2	Sr	.0575	.2418	102.6	.3209	.3339	.6661	7.95	8.55
3	K	.0587	.2752	103.3	.3554	.3107	.6893	9.51	9.20
4	K	.0591	.2745	101.2	.3623	.3120	.6880	9.42	8.95
5	K	.0582	.2772	102.5	.3596	.3067	.6933	9.81	9.38
Mean					.3444				8.97
									corr.to .1772
6	Sr	.0788	.2169	199.2	.1641	.4341	.5659	4.00	4.33
7	Sr	.0787	.2230	203.6	.1636	.4264	.5736	4.16	4.51
8	Sr	.0858	.2529	205.0	.1823	.4170	.5830	4.46	4.33
9	K	.0836	.2589	204.5	.1848	.4049	.5951	4.84	4.64
10	K	.0863	.2663	203.6	.1910	.4057	.5943	4.81	4.46
Mean					.1772				4.45

TABLE XII

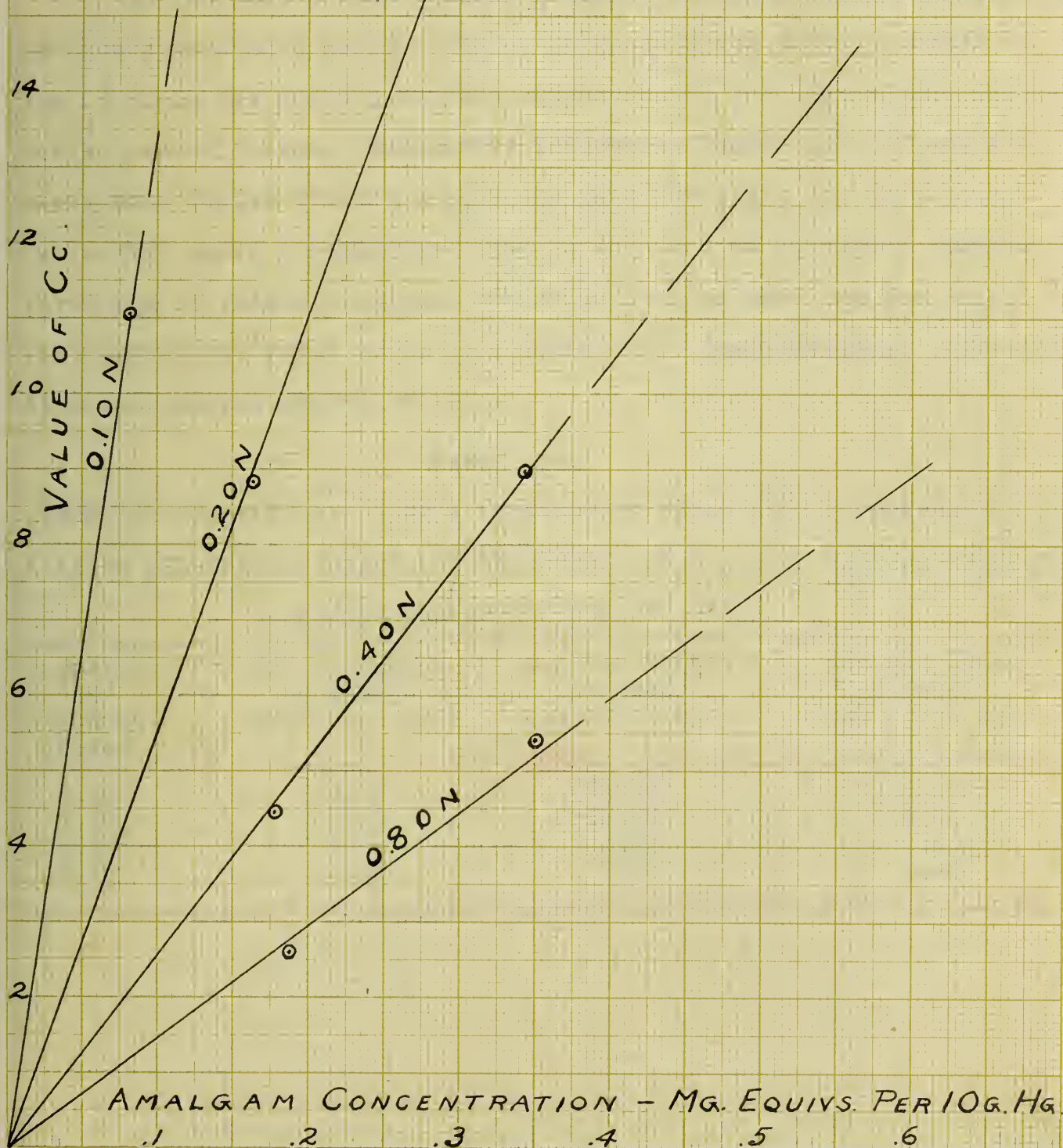
MIXED AQUEOUS PHASE 0.80N

									corr.to .3522
1	Sr	.0759	.2353	104.1	.3299	.4051	.5949	4.84	5.17
2	Sr	.0766	.2434	101.5	.3478	.3990	.6010	5.03	5.10
3	Sr	.0787	.2615	109.0	.3441	.3881	.6119	5.41	5.53
4	K	.0804	.2853	105.5	.3820	.3728	.6272	6.01	5.53
5	K	.0779	.2716	107.9	.3570	.3771	.6229	5.83	5.76
Mean					.3522				5.42
									corr.to .1877
6	Sr	.1106	.2313	203.0	.1866	.5019	.4981	2.64	2.66
7	Sr	.1194	.2336	204.3	.1916	.5187	.4813	2.38	2.34
8	Sr	.1118	.2402	204.0	.1912	.4953	.5047	2.74	2.68
9	K	.1198	.2293	215.8	.1795	.5242	.4758	2.32	2.43
10	K	.1083	.2363	197.7	.1930	.4914	.5086	2.81	2.73
11	K	.1083	.2267	201.4	.1842	.5018	.4982	2.64	2.69
Mean					.1877				2.59

FIG. 3

SHOWING VALUE OF CC AS A FUNCTION
OF AMALGAM CONCENTRATION AT
DIFFERENT TOTAL SALT CONCENTRATIONS.

EQUIVALENT PROPORTIONS OF
K AND SR IN AQUEOUS PHASE.
TEMP. 40°C.



the heat of the interactions by means of the van't Hoff equation for different salt concentrations and some specific amalgam concentration, and also for different amalgam concentrations and some specific total salt concentration, assuming this heat effect to be constant over that temperature range. The heats of the interactions will be referred to later.

In the case of the aqueous solution of 0.20N concentration, experiments were made at 15°C, 20°C, 25°C, 30°C and 40°C, in order to see if there was any appreciable difference in the heat of the interaction over different temperature intervals. Tables XIV, XV and XVI along with Tables III and X show the data necessary for this study. Table XVII shows a summarized form of the data at different temperatures and at specific amalgam concentrations as obtained from Fig.5. Fig.6 shows the value of C_c as a function of temperature at different specific amalgam concentrations.

TABLE XIII

SHOWING THE VALUE OF C_c AS A FUNCTION OF TOTAL SALT CONCENTRATION AT A FIXED (EQUIVALENT) SALT CONCENTRATION RATIO AND AT VARIOUS SPECIFIC AMALGAM CONCENTRATIONS AT 40°C.

Normality of Aqueous Phase	0.1 mg.equiv. of metal per 10 g. Hg	0.2 mg. equiv. of metal per 10 g. Hg	0.3 mg. equiv. of metal per 10 g. Hg
0.10	13.40	(25.90)	
0.20	5.50	11.00	16.55
0.40	2.55	5.15	7.80
0.80	1.45	2.95	4.45

FIG. 4

SHOWING VALUE OF CC AS A FUNCTION
OF TOTAL SALT CONCENTRATION
AT DIFFERENT AMALGAM CONCENTRATIONS.

EQUIVALENT PROPORTIONS OF K
AND SR IN AQUEOUS PHASE.
TEMP. 40°C.

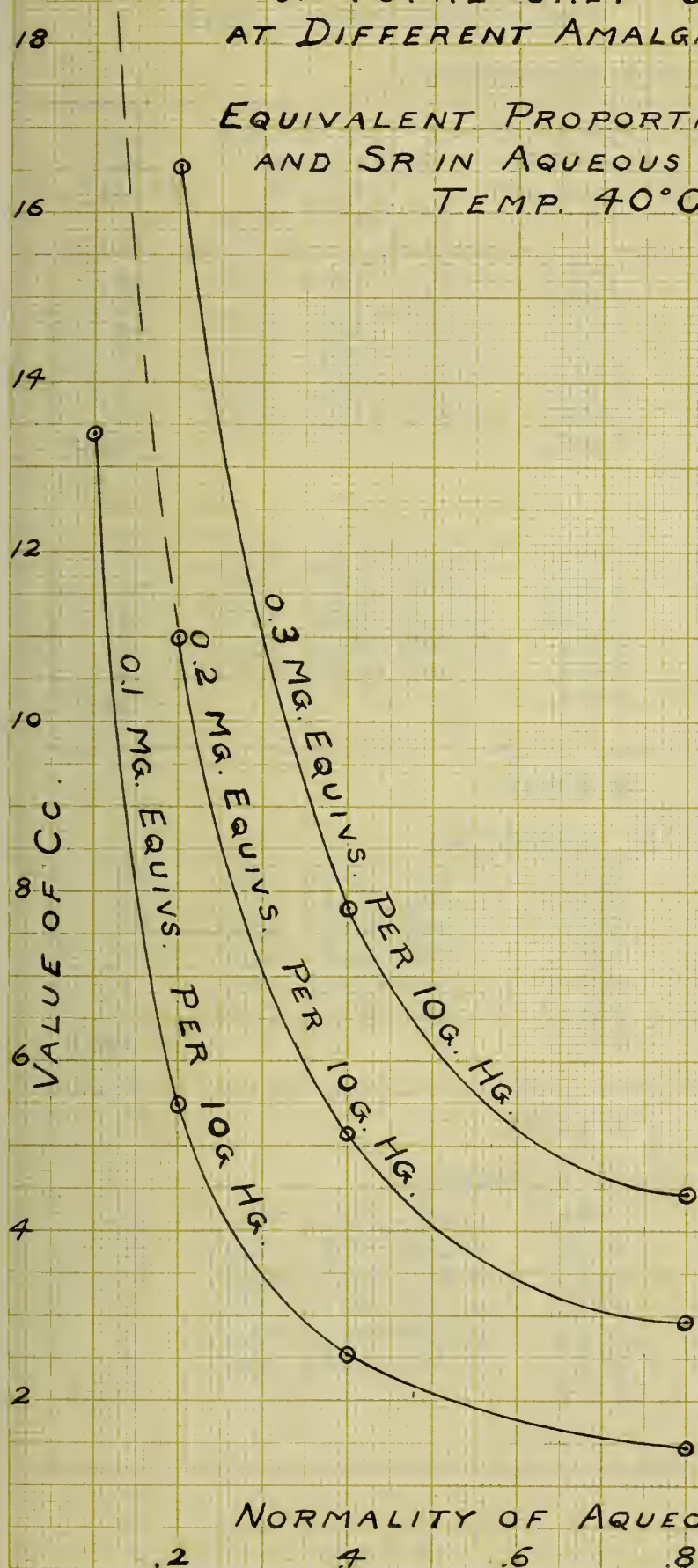


TABLE XIV

MIXED AQUEOUS PHASE 0.20N

KCl : 1/2 SrCl₂.

TEMPERATURE 30°C.

No.	Amal. at Start.	Analysis of the Equilibrium Amalgam			Milli-equivs. of Metals per 10 g. Hg	Amalgamated Metal Fractions.		Cc	Cc corr.to .3257 mg. equiv.
		K ₂ SO ₄	SrSO ₄	Hg		K	Sr		
1	Sr	.0547	.2970	104.9	.3681	.2802	.7198	12.21	10.81
2	Sr	.0531	.2712	104.3	.3414	.2920	.7080	11.06	10.50
3	Sr	.0542	.2765	103.8	.3500	.2921	.7079	11.06	10.30
4	K	.0496	.2327	108.4	.2864	.3104	.6896	9.54	10.82
5	K	.0501	.2393	103.9	.3061	.3064	.6936	9.84	10.47
6	K	.0500	.2311	102.2	.3023	.3129	.6871	9.35	10.08
Mean					.3257				10.50
									corr.to .1777
7	Sr	.0779	.2539	204.1	.1792	.3931	.6069	5.23	5.18
8	Sr	.0776	.2713	204.0	.1884	.3760	.6240	5.87	5.53
9	Sr	.0735	.2387	204.6	.1681	.3938	.6062	5.21	5.49
10	K	.0808	.2785	208.7	.1898	.3798	.6202	5.73	5.37
11	K	.0703	.2388	208.8	.1632	.3833	.6167	5.59	6.07
Mean					.1777				5.53

TABLE XV.

TEMPERATURE 20°C

corr.to
.1744

1	Sr	.1062	.2516	218.6	.1812	.4711	.5289	3.17	3.05
2	Sr	.1101	.2732	209.4	.2024	.4593	.5407	3.41	2.94
3	Sr	.1050	.2496	206.5	.1898	.4700	.5300	3.20	2.94
4	K	.1045	.2323	209.9	.1776	.4867	.5133	2.89	2.84
5	K	.0972	.1934	211.6	.1522	.5144	.4856	2.45	2.81
6	K	.0872	.1796	206.1	.1434	.5055	.4945	2.57	3.12
Mean					.1744				2.95

TABLE XVI

TEMPERATURE 15°C

corr.to
.1964

1	Sr	.1325	.2478	203.2	.2077	.5300	.4700	2.24	2.12
2	Sr	.1421	.2679	209.6	.2170	.5279	.4721	2.25	2.04
3	Sr	.1495	.3116	213.8	.2390	.5029	.4971	2.61	2.14
4	K	.1264	.1940	206.6	.1723	.5787	.4213	1.68	1.92
5	K	.1198	.1808	202.5	.1651	.5830	.4170	1.59	1.89
6	K	.1227	.2055	205.5	.1774	.5575	.4425	1.89	2.10
Mean					.1964				2.04

FIG. 5⁰ /

SHOWING VALUE OF CC AS A FUNCTION
OF AMALGAM CONCENTRATION AT
DIFFERENT TEMPERATURES.

EQUIVALENT PROPORTIONS OF K
AND SR IN AQUEOUS PHASE.
TOTAL NORMALITY -.20

16

14

12

VALUE OF CC.

10

8

6

4

2

TEMP. 40°C.

TEMP. 30°C.

TEMP. 25°C.

TEMP. 20°C.

TEMP. 15°C.

AMALGAM CONCENTRATION - MG. EQUIVS. PER 10G. HG

.1

.2

.3

.4

.5

.6

TABLE XVII

SHOWING THE VALUE OF C_c AS A FUNCTION OF TEMPERATURE AT A FIXED (EQUIVALENT) SALT CONCENTRATION RATIO BUT AT VARIOUS SPECIFIC AMALGAM CONCENTRATIONS FOR A TOTAL SALT CONCENTRATION OF 0.20 N.

Temp.	0.1 mg. equiv. of metal per 10 g. Hg	0.2 mg. equiv. of metal per 10 g. Hg	0.3 mg. equiv. of metal per 10 g. Hg
15°C	1.05	2.10	(3.15)
20°C	1.72	3.45	(5.10)
25°C	2.40	4.75	7.15
30°C	3.20	6.40	9.55
40°C	5.50	11.00	16.55

4. EFFECT OF VARYING THE CONCENTRATION RATIO OF THE SALTS AT A FIXED TOTAL SALT CONCENTRATION AND AT VARIOUS AMALGAM CONCENTRATIONS. Tables XVIII(a), XVIII(b), XVIII(c), XVIII(d), XIX(a), XIX(b), XIX(c), XIX(d), XX(a), XX(b), XX(c) and XX(d) give the data obtained at total salt concentrations of 0.20N, 0.40N and 0.80N respectively, upon varying the ratio of the salts. Solutions containing two and four equivalents of each salt to the other were studied. It was noted that here also for a fixed total salt concentration and fixed salt ratio that the value of C_c was a linear function of amalgam concentration as was shown previously for solutions containing equivalent proportions of salts (see Fig. 1). Fig. 7 shows the results of this study and Table XXI gives a summarized form of the data obtained showing the value of C_c as a function of the change of the ratio of the salts at total fixed salt concentrations and at specific amalgam concentrations, as obtained from Fig. 7.

It will be noticed that the values of C_c at any one specific amalgam concentration for any total salt concentration for a ratio of four equivalents of potassium salt to one equivalent of strontium salt

FIG. 6

SHOWING VALUE OF CC AS A FUNCTION
OF TEMPERATURE AT
DIFFERENT AMALGAM CONCENTRATIONS.

EQUIVALENT PROPORTIONS OF K
AND SR IN AQUEOUS PHASE.
TOTAL NORMALITY - 0.20

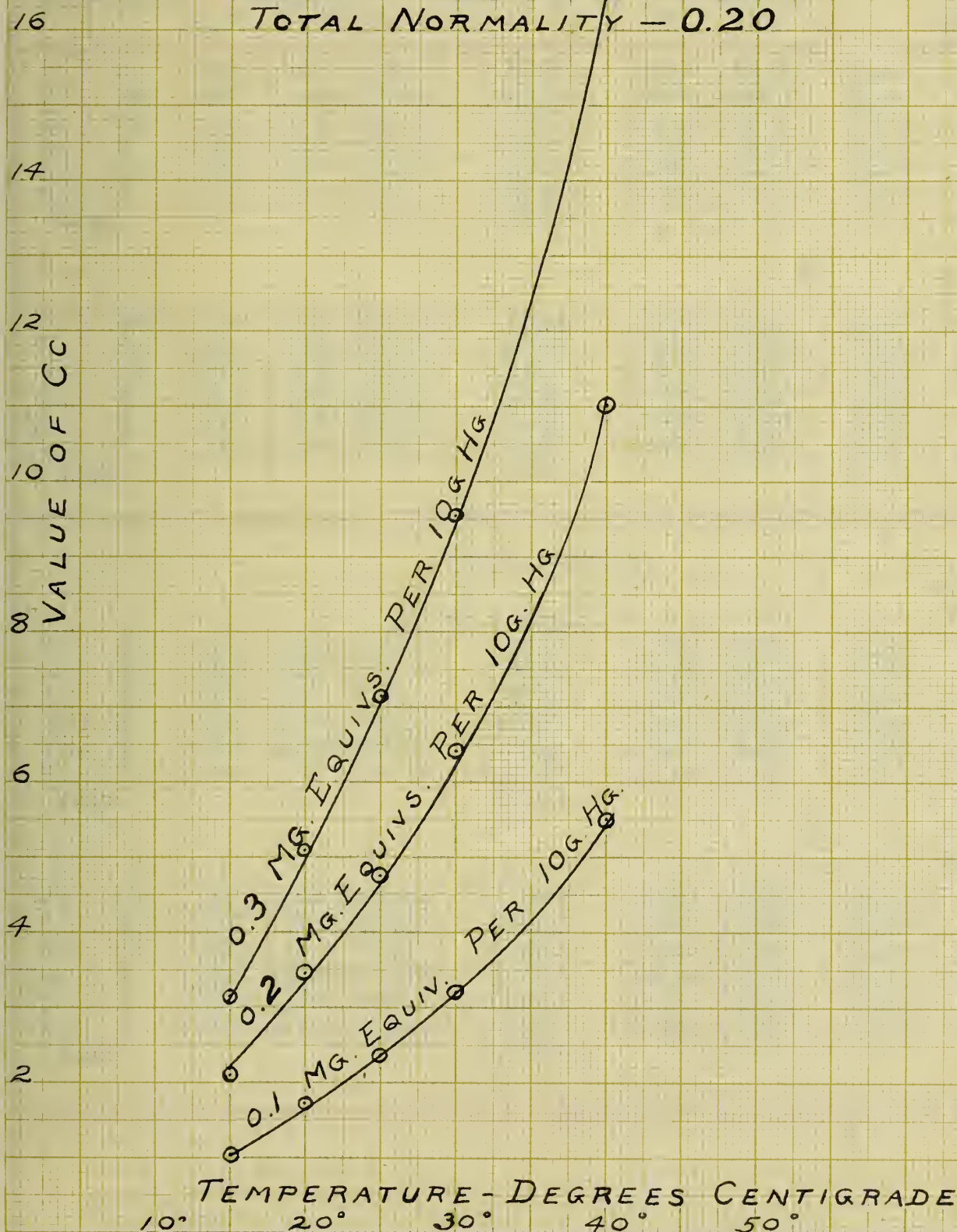


TABLE XVIII(a).

MIXED AQUEOUS PHASE 0.20N

8 KCl : SrCl₂.

TEMPERATURE 25°C.

No.	Amal. at Start.	Analysis of the Equilibrium Amalgam.			Milli-equivs. of Metals per 10 g. Hg	Amalgamated Metal Fractions		Cc	Cc corr.to .2781 mg.equiv.
		K ₂ SO ₄	SrSO ₄	Hg		K	Sr		
1	Sr	.1198	.1422	103.1	.2836	.6400	.3600	6.25	6.13
2	Sr	.1237	.1508	107.2	.2855	.6336	.3664	6.49	6.33
3	Sr	.1299	.1749	103.5	.3280	.6103	.3897	7.44	6.30
4	K	.1095	.1207	96.5	.2667	.6568	.3432	5.66	5.92
5	K	.1066	.1165	100.7	.2477	.6587	.3413	5.59	6.28
6	K	.1051	.1162	96.1	.2572	.6563	.3437	5.67	6.12
Mean					.2781				6.18
									corr. to .1521
7	Sr	.1553	.1152	200.5	.1514	.7399	.2601	3.38	3.39
8	Sr	.1614	.1228	205.6	.1553	.7349	.2651	3.49	3.41
9	Sr	.1596	.1196	201.1	.1558	.7379	.2621	3.42	3.34
10	K	.1592	.1099	210.0	.1441	.7535	.2465	3.09	3.26
11	K	.1607	.1155	206.4	.1503	.7457	.2643	3.38	3.42
12	K	.1587	.1174	199.0	.1557	.7402	.2598	3.37	3.29
Mean					.1521				3.35

TABLE XVIII(b)

4 KCl : SrCl₂.corr.to
.2963

1	Sr	.0887	.1910	101.0	.3067	.4947	.5053	6.61	6.40
2	Sr	.0886	.2027	102.7	.3143	.4795	.5205	7.24	6.83
3	Sr	.0859	.1971	100.1	.3130	.4792	.5208	7.26	6.87
4	K	.0850	.1731	100.4	.2851	.5088	.4912	6.07	6.32
5	K	.0869	.1824	105.9	.2812	.5011	.4989	6.36	6.64
6	K	.0843	.1703	101.9	.2767	.5105	.4895	6.01	6.44
Mean					.2963				6.59
									corr.to .1707
7	Sr	.1301	.1994	202.4	.1810	.5791	.4209	4.02	3.79
8	Sr	.1377	.2188	212.5	.1865	.5704	.4296	4.23	3.87
9	Sr	.1266	.1847	204.7	.1693	.5909	.4091	3.75	3.78
10	K	.1224	.1668	204.3	.1575	.6074	.3926	3.40	3.69
11	K	.1257	.1725	203.8	.1630	.6056	.3944	3.44	3.60
12	K	.1302	.1855	210.4	.1671	.5969	.4031	3.62	3.70
Mean					.1707				3.74

TABLE XVIII(c).

MIXED AQUEOUS PHASE 0.20N

KCl : SrCl₂.

TEMPERATURE 25° C.

No.	Amal. at Start.	Analysis of the Equilibrium Amalgam			Milli-equivs. of Metals per 10 g. Hg	Amalgamated Metal Fractions		Cc	Cc corr.to .1614 mg.equiv.
		K ₂ SO ₄	SrSO ₄	Hg		K	Sr		
1	Sr	.0484	.2733	203.2	.1737	.2718	.7282	4.92	4.58
2	Sr	.0465	.2630	205.2	.1656	.2719	.7281	4.92	4.80
3	Sr	.0476	.2773	206.0	.1731	.2662	.7338	5.18	4.83
4	K	.0459	.2503	203.9	.1595	.2787	.7213	4.64	4.70
5	K	.0456	.2513	213.8	.1524	.2771	.7229	4.71	4.98
6	K	.0426	.2227	202.4	.1439	.2872	.7128	4.32	4.86
Mean					.1614				4.79
									corr.to .0923
7	Sr	.0677	.2883	402.5	.0973	.3312	.6688	3.05	2.90
8	Sr	.0719	.2795	409.5	.0945	.3519	.6481	2.62	2.56
9	Sr	.0858	.4008	421.5	.1269	.3110	.6890	3.56	2.60
10	K	.0669	.2492	409.5	.0849	.3613	.6387	2.45	2.66
11	K	.0590	.2078	403.5	.0729	.3747	.6253	2.23	2.83
12	K	.0592	.2257	406.5	.0771	.3565	.6435	2.53	3.03
Mean					.0923				2.76

TABLE XVIII(d).

KCl : 2 SrCl₂.

									corr.to .1788
1	Sr	.0541	.6085	405.1	.1789	.1580	.8420	5.62	5.62
2	Sr	.0587	.7952	420.3	.2220	.1350	.8650	7.58	6.12
3	Sr	.0528	.6114	407.9	.1781	.1541	.8459	5.94	5.98
4	K	.0454	.5659	410.2	.1629	.1443	.8552	6.79	7.45
5	K	.0463	.5264	411.3	.1522	.1566	.8434	5.73	6.73
Mean					.1788				6.38
									corr.to .0786
6	Sr	.0367	.2656	396.3	.0837	.2259	.7741	2.53	2.38
7	Sr	.0304	.2391	399.2	.0740	.2122	.7878	2.91	3.09
8	Sr	.0328	.2802	397.2	.0863	.1978	.8022	3.42	3.12
9	K	.0317	.2411	400.9	.0746	.2167	.7833	2.78	2.93
10	K	.0329	.2417	393.3	.0765	.2234	.7766	2.59	2.68
11	K	.0325	.2443	397.6	.0763	.2192	.7808	2.71	2.79
Mean					.0786				2.83

TABLE XIX(a).

MIXED AQUEOUS PHASE 0.40N

8 KCl : SrCl₂.

TEMPERATURE 25° C.

No.	Amal. at Start.	Analysis of the Equilibrium Amalgam			Milli-equivs. of Metals per 10 g. Hg	Amalgamated Metal Fractions		Cc	Cc corr.to .3208 mg. equiv.
		K ₂ SO ₄	SrSO ₄	Hg		K	Sr		
1	Sr	.1615	.1282	103.2	.3149	.7267	.2733	3.68	3.75
2	Sr	.1616	.1297	100.0	.3267	.7241	.2759	3.74	3.68
3	Sr	.1636	.1363	100.7	.3338	.7167	.2843	3.93	3.78
4	K	.1600	.1256	101.6	.3153	.7287	.2713	3.63	3.70
5	K	.1640	.1214	107.8	.2972	.7401	.2599	3.37	3.64
6	K	.1765	.1491	108.4	.3367	.7139	.2861	3.99	3.80
Mean					.3208				3.73
									corr.to .1790
7	Sr	.2180	.1042	201.6	.1805	.8153	.1847	1.98	1.96
8	Sr	.2257	.1150	204.9	.1875	.8055	.1945	2.13	2.04
9	Sr	.2178	.1052	210.2	.1735	.8136	.1864	2.00	2.06
10	K	.2182	.1011	206.2	.1749	.8199	.1801	1.91	1.96
11	K	.2215	.1030	204.8	.1788	.8193	.1807	1.92	1.92
Mean					.1790				1.99

TABLE XIX(b).

4 KCl : SrCl₂.corr.to
.3035

No.	Sr	Analysis of the Equilibrium Amalgam			Milli-equivs. of Metals per 10 g. Hg	Amalgamated Metal Fractions		Cc	Cc corr.to .1595
		K ₂ SO ₄	SrSO ₄	Hg		K	Sr		
1	Sr	.1230	.1907	101.5	.3435	.5764	.4236	4.08	3.62
2	Sr	.1162	.1620	101.8	.3045	.6021	.3979	3.51	3.50
3	Sr	.1204	.1715	102.2	.3178	.5966	.4034	3.63	3.48
4	K	.1200	.1578	105.9	.2925	.6159	.3841	3.24	3.36
5	K	.1126	.1393	106.3	.2641	.6301	.3699	2.98	3.43
6	K	.1168	.1605	103.4	.2985	.6055	.3945	3.44	3.50
Mean					.3035				3.48
									corr.to .1595
7	Sr	.1651	.1428	203.3	.1696	.7091	.2909	1.85	1.74
8	Sr	.1593	.1416	201.5	.1673	.7036	.2964	1.92	1.83
9	Sr	.1685	.1464	203.3	.1735	.7081	.2919	1.86	1.71
10	K	.1465	.1082	203.7	.1404	.7407	.2593	1.51	1.72
11	K	.1522	.1254	202.5	.1537	.7190	.2810	1.74	1.80
12	K	.1598	.1253	210.1	.1523	.7287	.2713	1.64	1.72
Mean					.1595				1.75

TABLE XIX(c).

MIXED AQUEOUS PHASE 0.40N

KCl : SrCl₂.

TEMPERATURE 25° C.

No.	Amal. at Start.	Analysis of the Equilibrium Amalgam			Milli-equivs. of Metals per 10 g. Hg	Amalgamated Metal Fractions.		Cc	Cc corr.to .1495 mg.equiv.
		K ₂ SO ₄	SrSO ₄	Hg		K	Sr		
1	Sr	.0634	.2271	202.6	.1575	.3709	.6291	2.29	2.17
2	Sr	.0593	.2218	205.1	.1510	.3603	.6397	2.46	2.43
3	Sr	.0709	.2439	202.8	.1737	.3751	.6249	2.22	1.91
4	K	.0636	.2062	203.9	.1459	.3946	.6054	1.95	2.00
5	K	.0567	.1930	207.0	.1330	.3831	.6169	2.10	2.36
6	K	.0600	.1929	205.1	.1359	.3958	.6042	1.93	2.12
Mean					.1495				2.16
									corr.to .0854
7	Sr	.0858	.2279	393.7	.0880	.4424	.5576	1.43	1.39
8	Sr	.0993	.2461	397.8	.0961	.4598	.5402	1.28	1.14
9	Sr	.0904	.2203	401.6	.0855	.4640	.5360	1.25	1.25
10	K	.0857	.2088	396.6	.0821	.4636	.5364	1.25	1.30
11	K	.0835	.2057	396.2	.0807	.4614	.5386	1.26	1.33
12	K	.0854	.1999	394.7	.0799	.4738	.5262	1.17	1.25
Mean					.0854				1.28

TABLE XIX(d).

KCl : 2 SrCl₂.corr.to
.1748

1	Sr	.0418	.3436	209.7	.2013	.2044	.7956	3.17	2.75
2	Sr	.0371	.3336	204.1	.1988	.1904	.8096	3.72	3.26
3	Sr	.0344	.2837	198.5	.1754	.2032	.7968	3.22	3.21
4	K	.0364	.2578	212.2	.1518	.2291	.7709	2.45	2.82
5	K	.0332	.2556	202.9	.1560	.2150	.7850	2.83	3.17
6	K	.0360	.2739	204.9	.1657	.2175	.7825	2.76	2.92
Mean					.1748				3.02
									corr.to .0807
7	Sr	.0534	.2732	404.0	.0888	.2921	.7079	1.38	1.25
8	Sr	.0473	.2558	400.7	.0830	.2802	.7198	1.53	1.49
9	Sr	.0493	.2508	402.8	.0818	.2928	.7072	1.37	1.35
10	K	.0521	.2421	409.3	.0790	.3122	.6878	1.18	1.21
11	K	.0457	.2129	399.8	.0710	.3115	.6885	1.18	1.34
12	K	.0479	.2503	407.8	.0804	.2874	.7126	1.44	1.45
Mean					.0807				1.35

TABLE XX(a).

MIXED AQUEOUS PHASE 0.80N

8 KCl : SrCl₂.

TEMPERATURE 25°C.

No.	Amal. at Start.	Analysis of the Equilibrium Amalgam			Milli-equivs. of Metals per 10 g. Hg	Amalgamated Metal Fractions.		Cc	Cc corr.to .3166 mg.equiv.
		K ₂ SO ₄	SrSO ₄	Hg		K	Sr		
1	Sr	.2074	.1025	105.8	.3306	.8101	.1899	2.06	1.98
2	Sr	.2043	.1015	104.3	.3308	.8093	.1907	2.07	1.99
3	Sr	.2045	.1067	105.5	.3327	.8016	.1984	2.20	2.09
4	K	.2041	.0927	107.0	.3133	.8228	.1772	1.86	1.88
5	K	.1888	.0899	103.5	.3041	.8158	.1842	1.97	2.05
6	K	.1892	.0842	107.2	.2881	.8255	.1745	1.82	2.00
Mean					.3166				2.00
									corr.to .1772
7	Sr	.2766	.0843	207.8	.1971	.8738	.1262	1.18	1.06
8	Sr	.2672	.0764	203.7	.1913	.8807	.1193	1.09	1.01
9	Sr	.2614	.0796	206.4	.1874	.8737	.1263	1.17	1.11
10	K	.2344	.0599	207.3	.1613	.8917	.1083	0.97	1.06
11	K	.2358	.0608	201.6	.1671	.8911	.1089	0.97	1.03
12	K	.2210	.0611	201.4	.1590	.8842	.1158	1.05	1.17
Mean					.1772				1.07

TABLE XX(b).

4 KCl : SrCl₂.corr.to
.2988

1	Sr	.1459	.1438	98.5	.3291	.6814	.3186	2.20	2.00
2	Sr	.1457	.1414	100.4	.3199	.6849	.3151	2.15	2.01
3	Sr	.1123	.0790	101.2	.2125	.7479	.2503	1.42	2.00
4	K	.1528	.1486	98.1	.3438	.6843	.3157	2.16	1.88
5	K	.1298	.1201	94.5	.2963	.6951	.3049	2.02	2.04
6	K	.1392	.1241	101.3	.2912	.7029	.2971	1.93	1.98
Mean					.2988				1.99
									corr. to .1831
7	Sr	.2219	.1403	203.0	.2007	.7694	.2306	1.25	1.14
8	Sr	.1991	.1085	198.1	.1750	.7948	.2052	1.04	1.09
9	Sr	.2274	.1355	202.2	.2020	.7797	.2203	1.16	1.05
10	K	.1862	.1053	204.3	.1608	.7887	.2113	1.08	1.23
11	K	.2088	.1092	207.1	.1731	.8012	.1988	0.99	1.05
12	K	.2183	.1270	207.8	.1872	.7837	.2163	1.13	1.10
Mean					.1831				1.11

TABLE XX(c).

MIXED AQUEOUS PHASE 0.80N

KCl : SrCl₂.

TEMPERATURE 25° C.

No.	Amal. at Start.	Analysis of the Equilibrium Amalgam.			Milli-equivs. of Metals per 10 g. Hg	Amalgamated Metal Fractions		Cc	Cc corr.to .3132 mg. equiv.
		K ₂ SO ₄	SrSO ₄	Hg		K	Sr		
1	Sr	.0568	.2057	105.8	.2734	.3680	.6320	2.34	2.68
2	Sr	.0596	.2283	104.8	.3026	.3554	.6446	2.56	2.65
3	Sr	.0631	.2769	103.4	.3615	.3243	.6757	3.21	2.78
4	K	.0564	.2195	99.8	.3043	.3512	.6488	2.63	2.70
5	K	.0551	.2334	97.8	.3244	.3321	.6679	3.03	2.92
Mean					.3132				2.75
									corr.to .1817
6	Sr	.1004	.2344	201.1	.1843	.4747	.5253	1.17	1.15
7	Sr	.0952	.2448	205.6	.1827	.4505	.5495	1.35	1.34
8	Sr	.0937	.2469	202.8	.1856	.4449	.5551	1.40	1.37
9	K	.0904	.2427	214.3	.1716	.4402	.5598	1.44	1.52
10	K	.0945	.2492	209.6	.1801	.4443	.5557	1.41	1.42
11	K	.0980	.2438	203.7	.1856	.4588	.5412	1.29	1.26
Mean					.1817				1.34

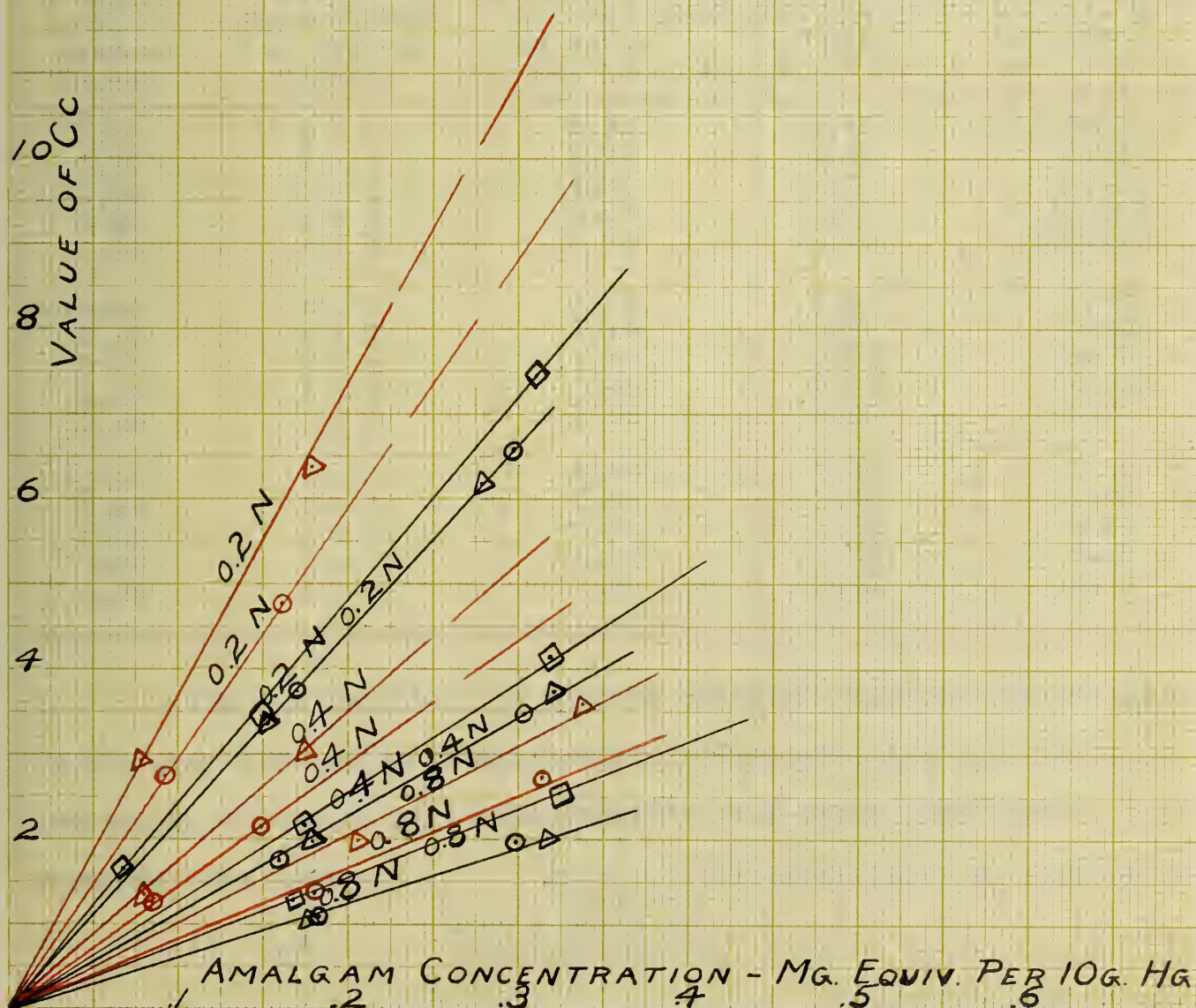
TABLE XX(d).

KCl : 2 SrCl₂.corr.to
.3371

1	Sr	.0323	.2769	100.3	.3377	.1974	.8026	3.43	3.43
2	Sr	.0319	.2719	101.7	.3272	.1981	.8019	3.41	3.52
3	K	.0322	.2936	109.5	.3258	.1283	.8117	3.81	3.94
4	K	.0328	.2956	100.3	.3584	.1893	.8107	3.77	3.54
Mean					.3371				3.60
									corr.to .2052
5	Sr	.0538	.3591	207.6	.2182	.2404	.7596	2.19	2.06
6	Sr	.0511	.3478	204.2	.2142	.2362	.7638	2.28	2.19
7	Sr	.0589	.3370	208.7	.2082	.2691	.7309	1.68	1.66
8	K	.0491	.3208	207.5	.1954	.2437	.7563	2.12	2.22
9	K	.0518	.3021	205.2	.1893	.2659	.7341	1.73	1.88
10	K	.0540	.3355	207.3	.2061	.2531	.7469	1.94	1.93
Mean					.2052				1.99

SHOWING VALUE OF CC AS A FUNCTION OF
AMALGAM CONCENTRATION AT
DIFFERENT TOTAL SALT CONCENTRATIONS
AND VARYING PROPORTIONS OF
K AND SR IN AQUEOUS PHASE.
TEMP. 25°C.

8KCL: SRCL₂ OR 4EQUIV. K: 1EQUIV. SR — Δ
4KCL: SRCL₂ OR 2EQUIV. K: 1EQUIV. SR — \circ
KCL: SRCL₂ OR 1EQUIV. K: 2EQUIV. SR — \circ
KCL: 2SRCL₂ OR 1EQUIV. K: 4EQUIV. SR — Δ
2KCL: SRCL₂ OR 1EQUIV. K: 1EQUIV. SR — \square



are identical with the values of C_c obtained for the same total salt concentration but with a ratio of two equivalents of potassium salt to one equivalent of strontium salt. But as the proportion of strontium salt is increased, a change in the value of C_c becomes more marked and the values obtained for a ratio of one equivalent of potassium salt to four equivalents of strontium salt are widely different from those obtained for other ratios of salts.

TABLE XXI

SHOWING THE VALUE OF C_c AS A FUNCTION OF THE CHANGE OF RATIO OF SALTS AT A FIXED TOTAL CONCENTRATION AND AT VARIOUS SPECIFIC AMALGAM

CONCENTRATIONS AT 25° C.

Normality of Aqueous Phase	Ratio: Equivs. K Salt to equivs. Sr Salt.	Value of C_c at amalgam conc. of:		
		0.1 mg. equiv. of metal per 10 g. Hg	0.2 mg. equiv. of metal per 10 g. Hg	0.3 mg. equiv. of metal per 10 g. Hg
0.20	4 : 1	2.22	4.45	6.65
0.20	2 : 1	2.22	4.45	6.65
0.20	1 : 1	2.40	4.75	7.15
0.20	1 : 2	2.95	5.90	(8.80)
0.20	1 : 4	3.70	7.40	(10.95)
0.40	4 : 1	1.15	2.30	3.45
0.40	2 : 1	1.15	2.30	3.45
0.40	1 : 1	1.30	2.60	3.90
0.40	1 : 2	1.45	2.90	(4.35)
0.40	1 : 4	1.75	3.50	(5.25)
0.80	4 : 1	0.60	1.25	1.90
0.80	2 : 1	0.60	1.25	1.90
0.80	1 : 1	0.78	1.55	2.35
0.80	1 : 2	0.85	1.65	2.55
0.80	1 : 4	1.05	2.05	3.10

5. THE ION FRACTIONS IN AQUEOUS CHLORIDE SOLUTIONS OF POTASSIUM AND STRONTIUM MIXED IN EQUIVALENT PROPORTIONS, AND THE EFFECT OF INCREASING THE TOTAL SALT CONCENTRATION AT A FIXED (EQUIVALENT) SALT CONCENTRATION RATIO.

In the theoretical part, an expression,

$$K^+ = \frac{-a + \sqrt{a^2 + 4a}}{2}$$

has been developed, in which

$$a = \frac{Co (KSalt)^2}{Cc (SrSalt)c}.$$

Table VIII gives the values of Cc for the different total salt concentrations. It has also been pointed out that as soon as a value of Co is known, it will be possible to calculate the ion fractions in mixed equivalent chloride solutions of any total salt concentration.

(a). The Co Value.

In the study of the ionic relationships in the solutions of KCl and SrCl₂, mixed in equivalent proportions, seven different total salt concentrations were studied with an amalgam concentration of 0.20 milli-equivalents of metals per 10 grams of mercury, namely 0.05N, 0.10N, 0.20N, 0.40N, 0.80N, 1.60N and 3.00N. Fig. 2 shows the curve obtained by plotting the Cc values against total salt concentration using the known coordinates of these seven points. The equation of this curve may be found, and Co obtained from it by a mathematical extrapolation.

The most general form of an algebraic equation of the second degree in two variables, is

$$A'x^2 + B'y^2 + C'xy + D'x + E'y + F' = 0$$

$$\text{or } x^2 + A y^2 + B xy + C x + D y + E = 0.$$

By substituting concentration for y and Cc for x, for the five points corresponding to 0.05N, 0.10N, 0.20N, 1.60N and 3.00N, five simultaneous equations are obtained involving the five unknown constants, A, B, C, D and E. These equations have been solved and an equation obtained which also satisfies the coordinates of the two points corresponding to 0.40N and 0.80N concentrations. The equation expressing the Cc values as a function of the total salt concentration is

$$x^2 - 837 y^2 + 4252 xy - 97 x - 2115 y - 3145 = 0$$

$$\text{or } (Cc)^2 - 837(\text{conc.})^2 + 4252(Cc \times \text{conc.}) - 2115(\text{conc.}) - 97(Cc) - 3145 = 0.$$

When the concentration equals zero, then C_c equals 125. This is the desired C_o value.

(b).The Ion Fractions.

Calculations of the ion fractions are given in Table XXII, and Fig.8 shows the different ion fractions as functions of the total salt concentration. The KCl and $SrCl_2$ are mixed in equivalent proportions, yet the ion fraction of potassium is greatly in excess of the strontium ion fraction. As the total concentration is increased, the potassium ion fraction becomes greater and finally reaches a constant value at a total salt concentration of 1.60N.

With the usual methods of studying ionization, the greatest difficulty is encountered in attempting to ascertain the different ion concentrations in an aqueous solution of a single salt of the type of strontium chloride, and in fact, even in the case of a salt of the simplest type, it is only in the region of very dilute solutions that we have any satisfactory idea of the percentage ionization; it is simply assumed that the conductance ratio, modified by some function of the viscosity, gives the correct value for the ionization. In a salt, like strontium chloride, involving the possible existence of more types of ions, the conductance ratio tells us nothing concerning the concentration of either the Sr^{++} ion or the intermediate $SrCl^+$ ion. The intermediate ion hypothesis was advocated by Harkins in 1911 and, on the basis of a variety of assumptions, he has offered calculations of the concentrations of such ions in dilute solutions of Ag_2SO_4 , K_2SO_4 and Na_2SO_4 (61). But even the assumptions of Harkins lead to no very accurate idea of the ion concentrations in a salt of the type of $SrCl_2$.

It is of interest in this connection to consider the most di-

lute solution studied, 0.05N, and calculate the ion fractions from necessary conductivity and transference data assuming the Isohydic Principle to be valid at this concentration. The most reliable conductance data, that of Kohlrausch as recorded by A.A. Noyes and Falk (62), corrected when necessary to 25°C by the temperature equation of DeGuisne (63) and transference data recorded by Noyes and Falk (64) was used. The degree of ionization of SrCl_2 into Sr^{++} ion is

$$\alpha = \frac{n_{\text{Sr}^{++}} \Lambda_{\text{SrSalt}}}{\Lambda_{\text{Sr}^{++}}}, \text{ where } n_{\text{Sr}^{++}} \text{ is the}$$

transference number of the strontium ion, Λ_{SrSalt} , the conductance of the strontium salt at 0.05N and $\Lambda_{\text{Sr}^{++}}$ is the conductance of the strontium ion at infinite dilution. For KCl the conductance ratio, corrected for viscosity, was used where the Λ_0 is the very accurate value obtained by Washburn and Weiland (65). Assuming the Isohydic Principle to be valid, a potassium ion fraction of .693 was obtained as compared to .889 by the distribution method. The results of the distribution method are based on the assumption that the fugacities of only the two ion species, potassium and strontium, hydrated and salted to different degrees, are measured by this method. If the fugacity of the intermediate SrCl^+ ion is also being measured, then the Sr^{++} ion fraction must necessarily be even smaller and the deviation of the ion fraction values obtained from the usual methods of studying ionization and the new distribution method would be far greater.

TABLE XXII

SHOWING THE VALUES OF THE CALCULATED ION FRACTIONS IN AQUEOUS KCl AND SrCl_2 SOLUTIONS MIXED IN EQUIVALENT PROPORTIONS AT 25°C .

Normality of Mixed Aqueous Solution.	Co	Cc	Calculated Ion Fractions	
			K^+	Sr^{++}
0.00	125.	125.	.666	.333
0.05	125	23.40	.889	.111
0.10	125	9.95	.946	.054
0.20	125	4.75	.973	.027
0.40	125	2.60	.985	.015
0.80	125	1.55	.991	.009
1.60	125	1.28	.992	.008
3.00	125	1.35	.992	.008

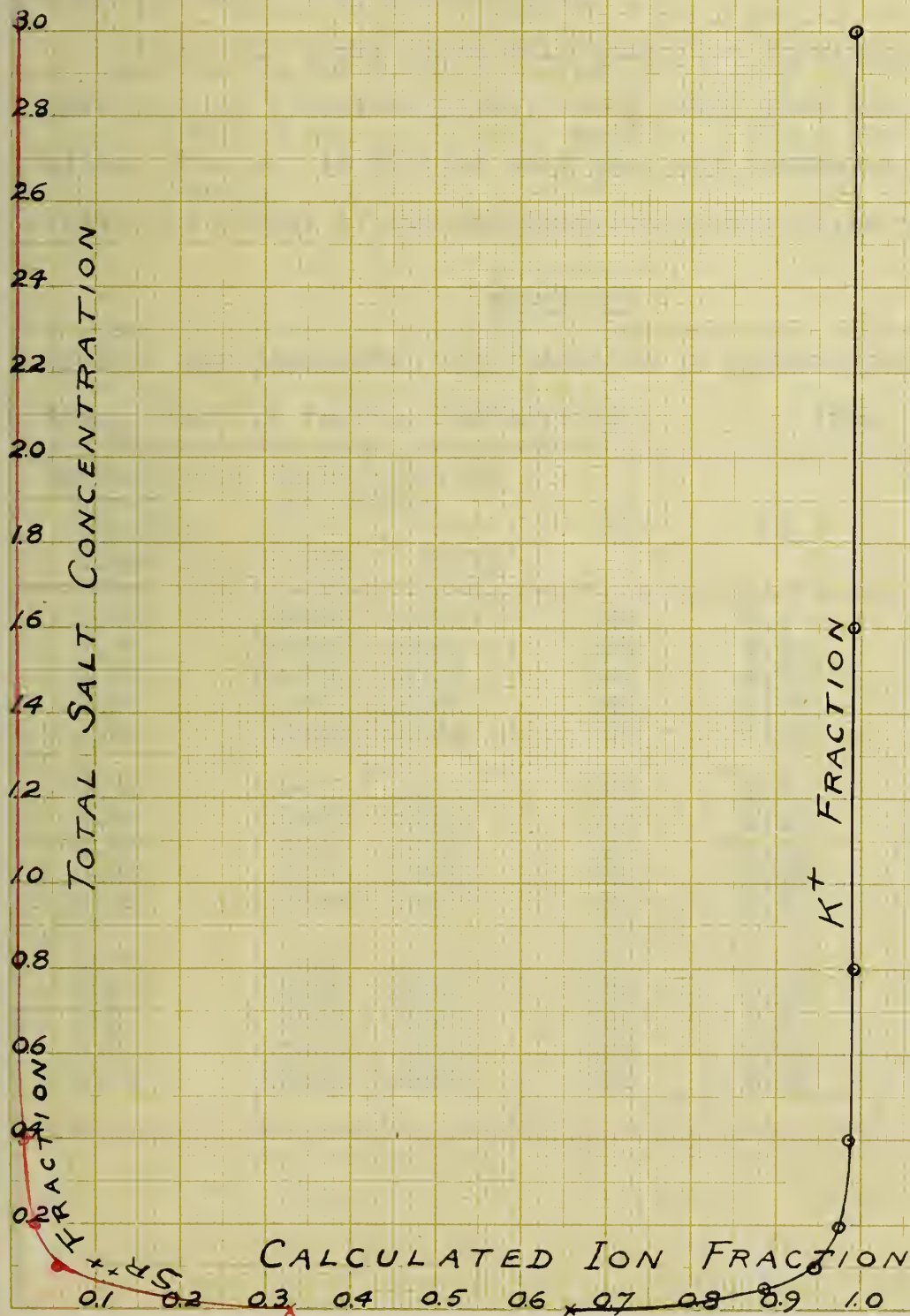
6. EFFECT OF THE TEMPERATURE ON THE ION FRACTIONS IN AQUEOUS CHLORIDE SOLUTIONS MIXED IN EQUIVALENT PROPORTIONS. Table XIII gives the necessary Cc values obtained at 40°C . The most dilute solution studied at this temperature was 0.10N while at 25°C the most dilute solution studied was 0.05N. The most concentrated solution studied at this temperature was 0.80N while at 25°C the most concentrated solution studied was 3.00N. Use of the mathematical method of extrapolation at 25°C showed that the Cc values for both 0.05N and 3.00N were very important in determining the value of Co so it does not seem advisable to offer any ion calculations for this temperature in view of the small range of concentration studied. The effect of temperature on the Cc values has already been discussed.

7. IONIC RELATIONSHIPS IN MIXED CHLORIDE SOLUTIONS OF VARYING SALT PROPORTIONS. It has already been shown that the equilibrium constant between the ions in the water and the metals in the mer-

FIG. 8

56.

SHOWING ION FRACTIONS OF POTASSIUM AND
STRONTIUM AS A FUNCTION OF TOTAL SALT
CONCENTRATION IN MIXED EQUIVALENT
AQUEOUS SOLUTIONS OF THEIR CHLORIDES.
TEMP. 25°C



cury must attain the same value regardless of the ratio of salts in the aqueous phase as long as the total concentration of metals in the mercurial phase is kept constant. With the mathematical method of extrapolation, a value of 125 was obtained for Co at a concentration of 0.20 milli-equivalents of metals per 10 grams of mercury. This value will be used in the ion fraction calculations in the cases where the salt ratio was changed.

Table XXV shows these calculated ion fractions and Table XXVI shows the ion fraction ratios, $\frac{K^+}{(KCl)}$ along with the salt mol-fraction ratios, $\frac{Sr^{++}}{(SrCl_2)}$. It will be seen that the potassium ion fraction is greatly in excess of the mol-fraction of KCl which supplies the ion.

TABLE XXV

SHOWING THE CALCULATED ION FRACTIONS IN AQUEOUS SOLUTIONS OF KCl AND $SrCl_2$ MIXED IN VARYING PROPORTIONS . TEMP. 25°C.

Normality of Mixed Aqueous Phase	Mol-fractions of Salts.		Co	Cc	Calculated Ion Fractions	
	KCl	$SrCl_2$			K^+	Sr^{++}
0.20	.8888	.1111	125	4.45	.995	.005
0.20	.8000	.2000	125	4.45	.989	.011
0.20	.6666	.3333	125	4.75	.973	.027
0.20	.5000	.5000	125	5.90	.920	.080
0.20	.3333	.6666	125	7.40	.782	.218
0.40	.8888	.1111	125	2.30	.998	.002
0.40	.8000	.2000	125	2.30	.993	.007
0.40	.6666	.3333	125	2.60	.985	.015
0.40	.5000	.5000	125	2.90	.958	.042
0.40	.3333	.6666	125	3.50	.872	.128
0.80	.8888	.1111	125	1.25	.999	.001
0.80	.8000	.2000	125	1.25	.997	.003
0.80	.6666	.3333	125	1.55	.991	.009
0.80	.5000	.5000	125	1.65	.975	.025
0.80	.3333	.6666	125	2.05	.967	.033

TABLE XXVI

SHOWING THE RATIO OF THE ION FRACTIONS AND THE RATIO OF THE SALT MOL-FRACTIONS IN MIXED CHLORIDE SOLUTIONS AT 25°C.		
Total Normality	Ratio:- KCl <hr/> SrCl ₂	Ratio:- K ⁺ <hr/> Sr ⁺⁺
0.20	8	199
0.20	4	90
0.20	2	36
0.20	1	12
0.20	0.5	3.6
0.40	8	499
0.40	4	142
0.40	2	66
0.40	1	23
0.40	0.5	6.8
0.80	8	999
0.80	4	332
0.80	2	110
0.80	1	39
0.80	0.5	29

8. THE MASS LAW IN MERCURIAL SOLUTIONS.

As has been

pointed out in the theoretical discussion, it is a necessary consequence of the mass law for each respective metal,

$$\frac{(Me)(Hg)^x}{(MeHg_x)} = K_m,$$

that C_c, or the value of the equilibrium expression

$$\frac{(SrHg)(KSalt)_c^2}{(K_{Hg})^2 (SrSalt)_c} = C_c$$

should be a linear function of the amalgam concentration. In Fig. 1, in which the values of C_c were plotted against amalgam concentration, the 0.20N curve is perfectly straight out to a concentration of about 0.40 milli-equivalents of metal per 10 grams of mercury; then

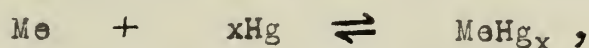
it begins to deviate slightly and from here on, the deviation becomes more and more pronounced. Figs. 9(a) and 9(b) show the variation of the mass action expression, K_m , with concentration for mercurial solutions of potassium and strontium where $\frac{C_c}{\text{conc.}} = kK_m$. The deviation begins at 0.15% for potassium and at 0.17% for strontium. It is evident then, that even if other equilibria do exist in the equilibrium amalgam, the composition of which determines the value of C_c , with the formation of compounds of which the mol-fractions are unknown, any errors thus introduced are compensating and the mass-action expression, with C_c values as a criterion, is affected by a constant factor up to a concentration of about 0.40 milli-equivalents per 10 grams of mercury.

9. THE AMALGAM AT EQUILIBRIUM.

The expression

$$\frac{\alpha N_K}{\alpha N_K + \beta N_{Sr}} = K^+ \quad \text{has been developed}$$

and it has been shown how the relative degrees of dissociation of the two hydrargyrides of strontium and potassium, in any equilibrium amalgam, may be obtained. Table XXVII gives the relative degrees of dissociation of the strontium-hydrargyride as compared to that for potassium hydrargyride, assuming the latter to be unity. This Table and Fig. 10 show that with increasing dilution of mercury, the free atoms of strontium decrease more rapidly in proportion to concentration than do the free atoms of potassium, showing that $\frac{\alpha}{\beta}$ has some other value than a constant. If the mass law holds for each respective metal independently of the other in the sense of the equation



$\frac{\alpha}{\beta}$ would have to be a constant in the equilibrium amalgams.

In the case of the aqueous phase, the concentration of strontium ion decreases much more rapidly in proportion to the concentra-

FIG. 9(a)

SHOWING THE VARIATION OF THE
MASS-ACTION EXPRESSION WITH
CONCENTRATION FOR MERCURIAL
SOLUTIONS OF POTASSIUM AND
STRONTIUM.

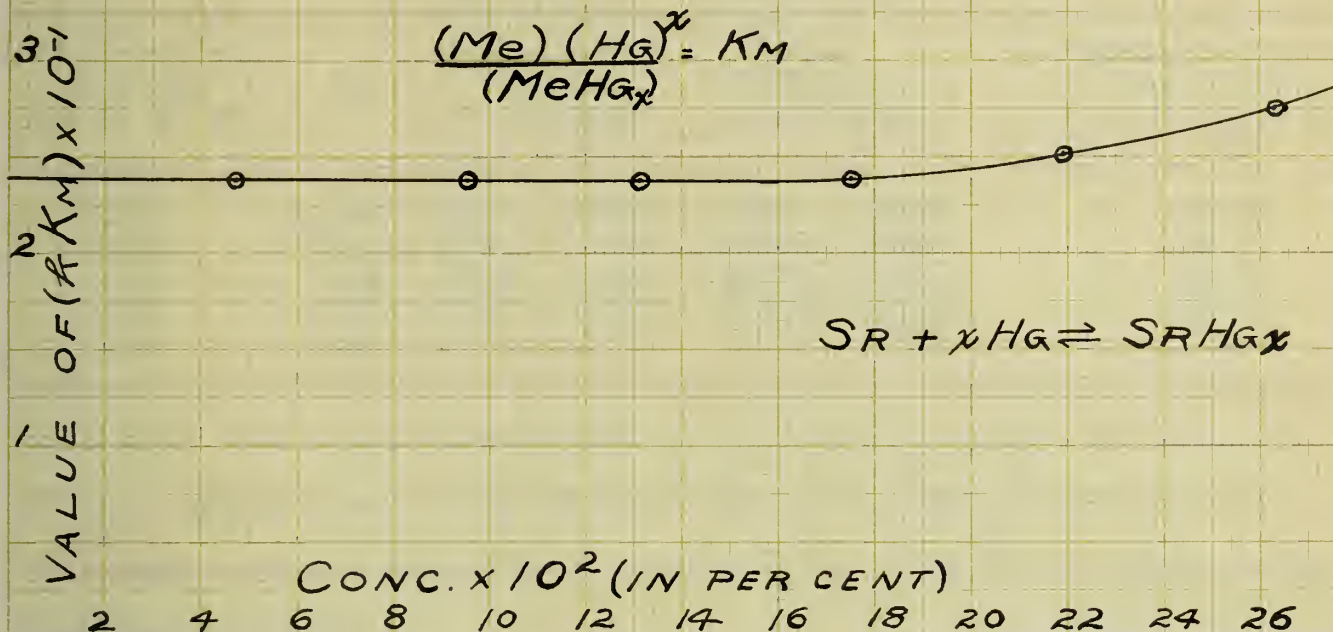


FIG. 9(b)

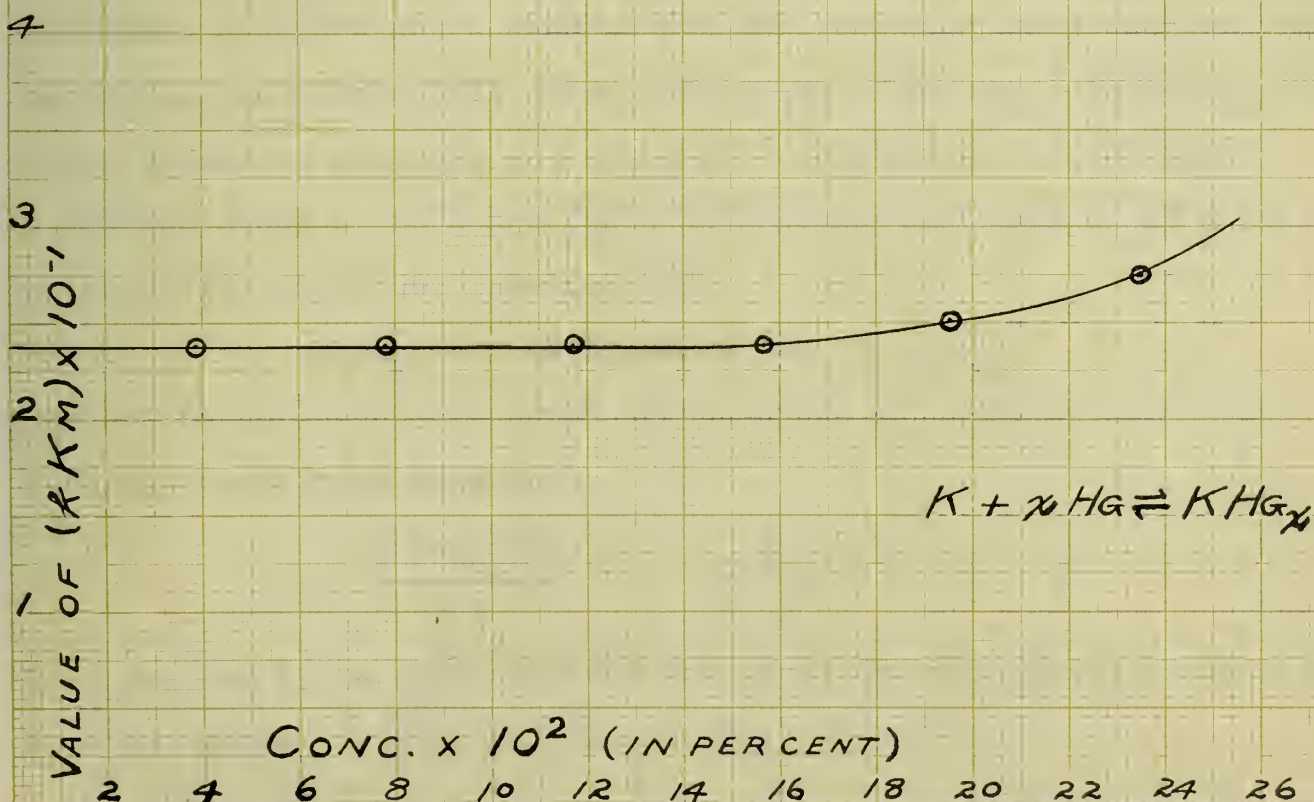


TABLE XXVII

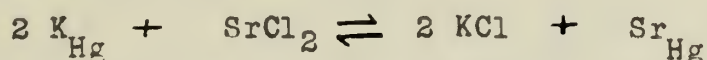
SHOWING THE FREE ATOM RELATIONS IN EQUILIBRIUM AMALGAMS OF DIFFERENT CONCENTRATIONS IN CONTACT WITH 0.20 N MIXED CHLORIDE SOLUTIONS. TEMP. 25°C.

Milli-equivs. of metal per 10 g. Hg	Cc	Amalgamated Metal Fractions		Total Number of Milli-atoms		Relative degrees of dissociation of hydrargyrides	
		K	Sr	K	Sr	K	Sr
0.50	11.90	.9055	.0945	.4137	.0432	1	54.9%
0.40	9.55	.8895	.1105	.3204	.0398	1	47.3
0.30	7.15	.8615	.1385	.2270	.0365	1	36.9
0.20	4.75	.8140	.1860	.1373	.0314	1	25.8
0.10	2.38	.7145	.2855	.0556	.0222	1	14.6

tion than does the potassium ion in proportion to the concentration of the potassium salt and now in a totally different environment, this same inherent property of strontium as compared to potassium is manifesting itself.

10. HEATS OF THE INTERACTIONS.

Table XVII gives the values of the equilibrium expression, Cc, for the interactions between different amalgams and a 0.20N mixed salt solution at different temperatures, and Table VIII gives the values of Cc for interactions between different amalgams and mixed salt solutions of 0.10N, 0.20N, 0.40N and 0.80N at 25°C and Table XIII gives this data at 40°C. The heats of the different interactions

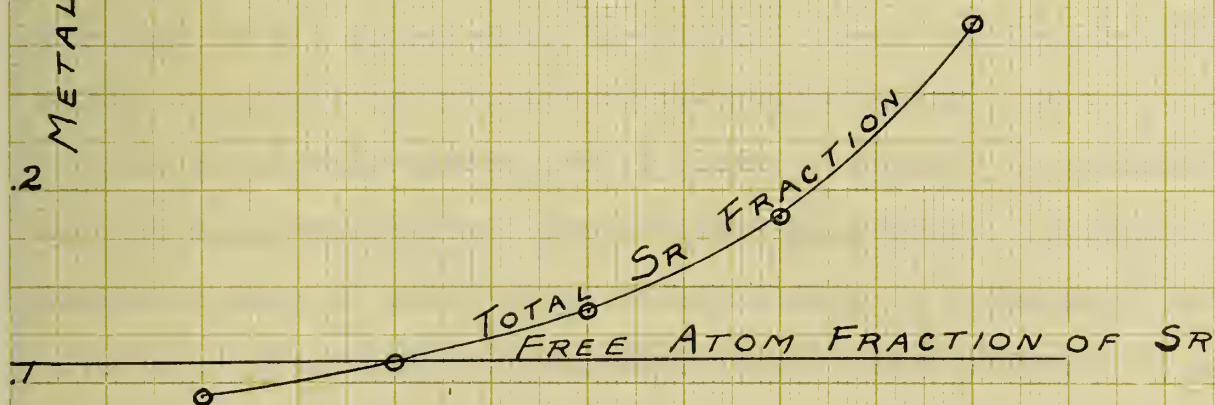
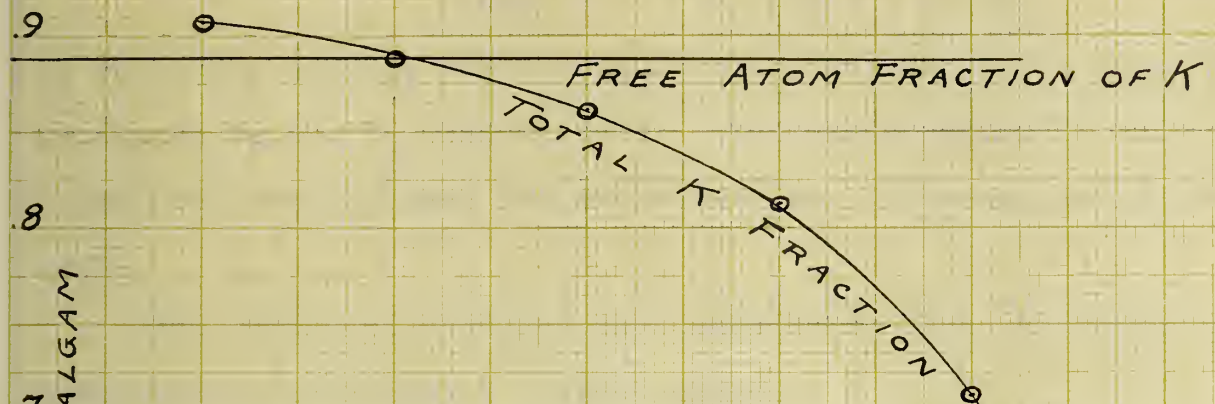


may now be determined from the values of Cc at different temperatures with the van't Hoff equation

$$\frac{d \log_e Cc}{dT} = \frac{Q}{RT^2}.$$

Q is assumed to be constant over the range of temperature studied or in other words $\frac{dQ}{dT} = Cp_2 - Cp_1 = \Delta Cp = 0.$

SHOWING A STUDY OF AMALGAMS IN
EQUILIBRIUM WITH A MIXED 0.20N SALT SOLUTION.



EQUILIBRIUM AMALGAM CONCENTRATION - MG. EQUIV. PER 10G. Hg

Integrating,

$$2.303 \log \frac{Cc_2}{Cc_1} = \frac{Q}{R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right]$$

in which Cc_2 and Cc_1 are the equilibrium values at the absolute temperatures, T_2 and T_1 respectively, R the gas constant in calories, and Q the heat evolved when the above reaction proceeds from right to left.

The effect of changing the temperature upon the value of Cc has been shown graphically in Figs.5 and 6.

Table XXVIII shows the heats of the different interactions as calculated. As determined, these heats are the algebraic sum of the heats of several reactions, dilution and ionization of salts, dilution and dissociation of hydrargyrides, etc., and independently, are of significance mainly with respect to the order of magnitude and direction. The reactions, as a whole, as represented, are exo-thermic.

However, a relative study of the heats of the different interactions leads to some definite ideas in regard to the heats of dilution of amalgams and also to heats of dilution of mixed salt solutions.

A comparison of the values of the interaction heats for any one solution and different amalgams shows that for the same solution, the heat is not affected by the amalgam concentration. In other words, the heat of dilution of the mixed amalgams of a concentration of 0.30 milli-equivalents per 10 grams of mercury to a concentration of 0.10 milli-equivalents per 10 grams of mercury, is zero. Here again the heat of dilution of such amalgams is a summation of heat effects of dissociation and association of the different hydrargyrides present; some of these reactions may be exo-thermic and others may be endo-thermic but a compensation occurs in such a manner that the

total heat effect is zero.

A comparison of the values of the interaction heats for any one amalgam and the different salt solutions shows that the heat of dilution of a mixed 0.80N salt solution to a 0.10N mixed salt solution is very considerable. The difference in the heat of the interaction of a 0.10N salt solution and a certain amalgam and that of an 0.80N salt solution and the same amalgam is some 7100 calories.

Fig.11 shows the variation of the heat of the interaction with total salt concentration for an amalgam of a concentration of 0.10 milli-equivalent of metal per 10 grams of mercury.

The data for 0.20N mixed solutions at the different temperature intervals, shows that Q is not strictly constant or that ΔC_p varies slightly over the temperature range studied.

TABLE XXVIII

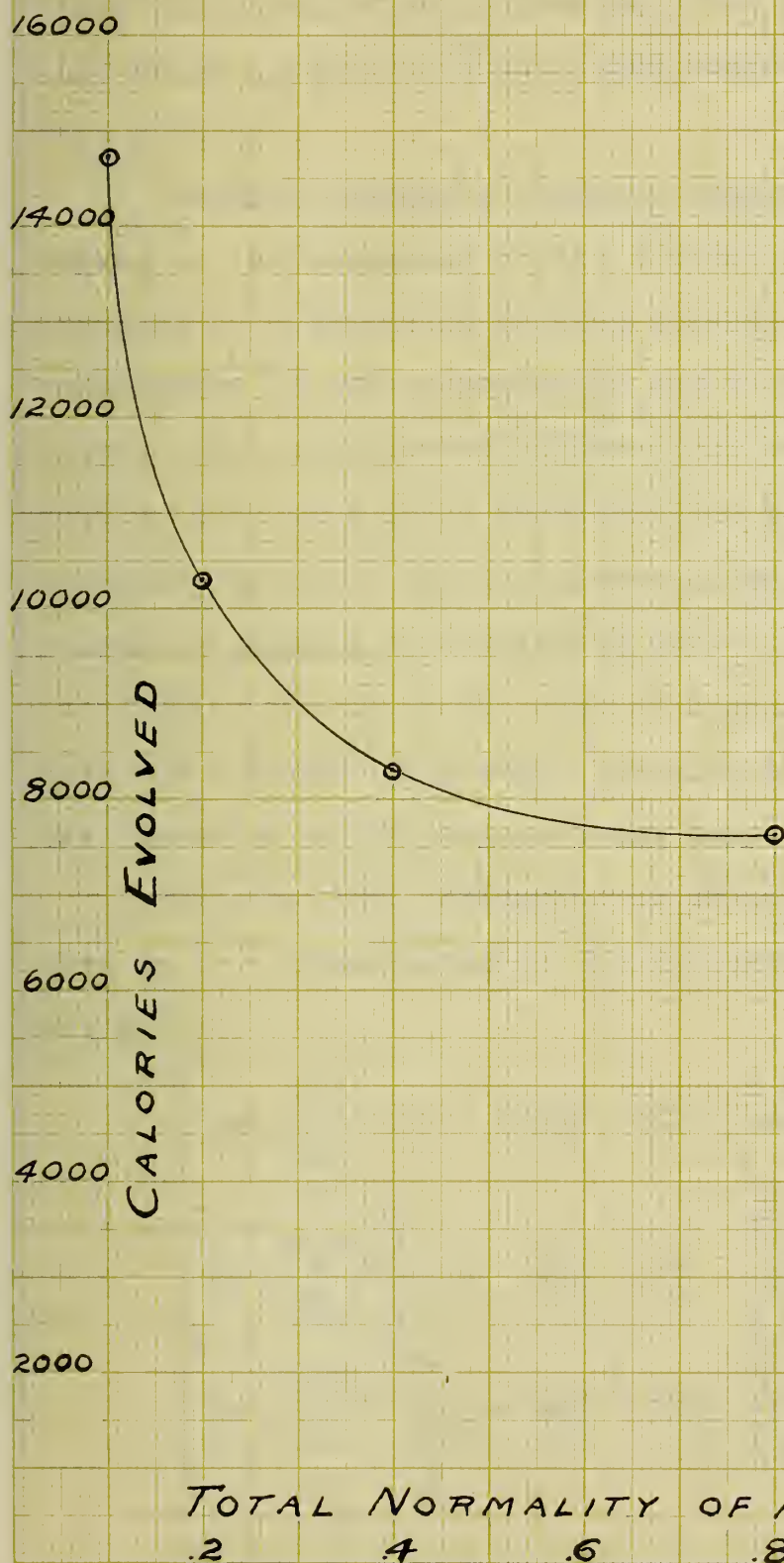
SHOWING THE HEATS OF THE INTERACTIONS.

(0.20N Mixed Salt Solution For Different Temperature Intervals)			
Calories Evolved between:	0.10 milli-equiv. per 10 g. Hg	0.20 milli-equiv. per 10 g. Hg	0.30 milli-equiv. per 10 g. Hg
15°C-20°C	16590	16600	16150
20°C-25°C	11230	11050	11700
25°C-30°C	10600	10680	10350
30°C-40°C	10100	10100	10250
(Temperature Interval of 25°C to 40°C for Different Solutions)			
Calories Evolved for Solutions of:			
0.10N	14750	11800	
0.20N	10300	10350	10325
0.40N	8320	8450	8300
0.80N	7650	7930	7880

FIG. 11

65.

SHOWING THE HEAT OF THE INTERACTION
AS A FUNCTION OF TOTAL SALT
CONCENTRATION.

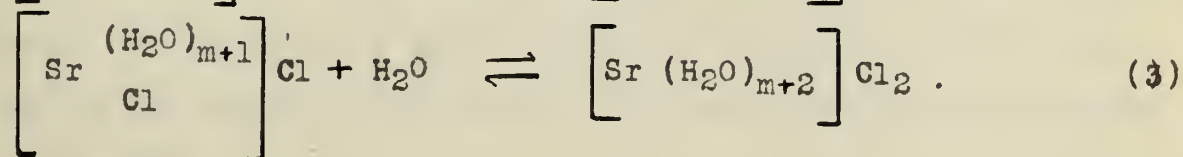
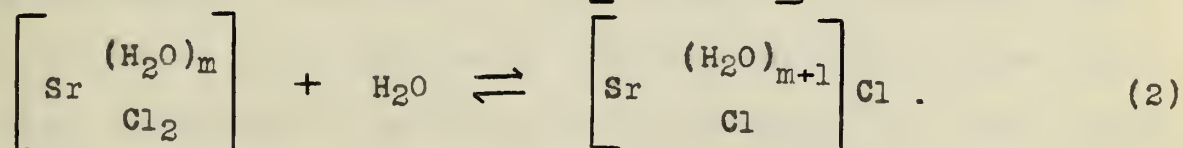
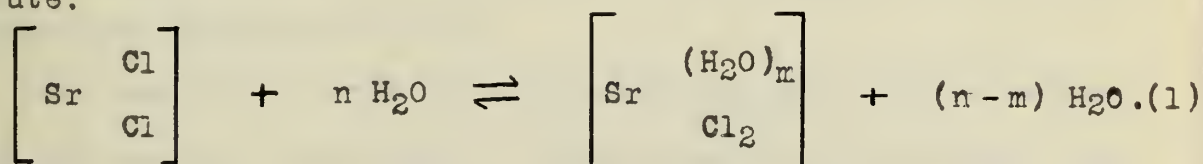


VI. DISCUSSION.

To recapitulate, this investigation has shown that in equivalent mixtures of potassium and strontium chlorides, the ion fraction of strontium decreases while the ion fraction of potassium correspondingly increases, with increasing total salt concentration. At 25°C, this holds true up to about 1.60N above which the ion fractions remain constant.

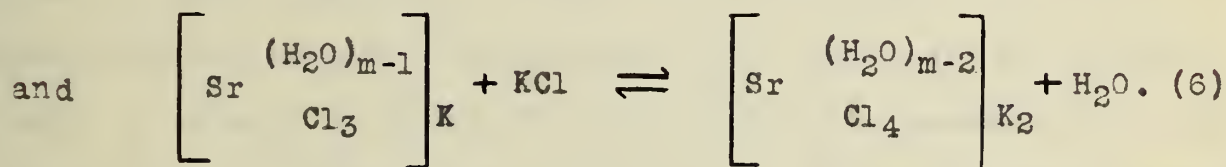
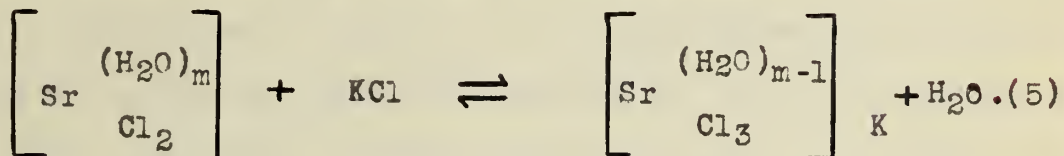
Kendall has quite recently emphasized the ideas of Werner in regard to the mechanism of the ionization process (66). "Ionization is preceded by combination between solvent and solute and is, indeed, a consequence of such combination and the two phenomena proceed in parallel." The formation of higher-order compounds between solvent and solute, with subsequent interpolation by the solvent, may occur to different extents, and the dissociation of these interpolated compounds is capable of furnishing ions of many different species. This is especially true in the case of mixed salt solutions, in which not only the solvent and a salt, but also the two salts may take part in the formation of the higher-order complexes.

Briefly, the ionization of strontium chloride may be considered to be a consequence of the following reactions between solvent and solute.





In the case of the simultaneous existence of these equilibria, molecules of potassium chloride and of strontium chloride may also take part in the formation of higher-order compounds, e.g.,



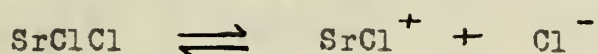
etc., etc., etc.

Omitting the molecules of water, then, such higher-order compounds would yield upon dissociation ions such as SrCl^+ , SrCl_3^- , SrCl_4^{--} , etc. Noyes and Falk (64), in consequence of a study of transference numbers in relation to the properties of salt solutions, have already referred to the probable existence of complex ions such as BaCl_4^{--} .

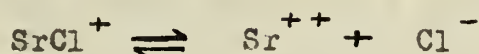
The relative possibility of formation of these higher-order compounds with the different metal elements as centers; the relative stabilities of such compounds, or their relative tendencies to dissociate largely determine whether there will exist a preponderance of the ionic species containing strontium in the complex; only these equilibria are represented above.

The results of this investigation are entirely in harmony with the existence of such ions as those predicted by Werner. The probability of the preponderance of complex ions derived from the higher-order compounds of strontium chloride rather than from those of potassium chloride would account for the relative low Sr^{++} ion concentration as compared with the K^+ ion concentration in mixtures of the two salts.

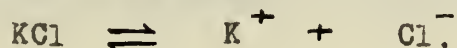
In 1911, Harkins advocated the application of the intermediate-ion hypothesis to salts, as well as to polybasic acids. And, in a series of investigations on the effect of salts on the solubility of other salts, evidence was furnished which would seem to show that the existence of such ions in solutions of uni-bivalent and bi-univalent salts can no longer be seriously questioned. In one of these investigations (67), the effect of KCl upon the solubility of SrCl_2 is studied. Although attention is called to the fact that, in the case of a salt as soluble as SrCl_2 , the effect might be masked by the specific solubility of SrCl_2 , the solubility is decreased by the addition of KCl. "The first step in the ionization of SrCl_2 is



and in very concentrated solutions this should be almost the only form of ionization". In the more dilute solutions the SrCl^+ will again ionize to give the simple Sr^{++} ion



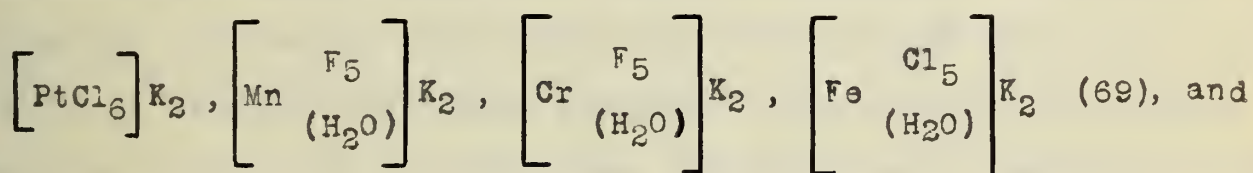
In the case of KCl, only one simple form of ionization is possible



Upon mixing solutions of these two salts, mass-action conceptions would lead us to expect the common Cl^- ion to force back the ionization of the intermediate SrCl^+ ion. These conceptions are also in accord with the results of this investigation, but attention should be called to the fact that such conceptions of ionization are not at all as recent as 1911, but were advanced long before by A. Werner. The intermediate SrCl^+ ion is nothing more than one of the ionic species resulting from the dissociation of the interpolation compound in reaction (2), with the molecules of water omitted; and furthermore, this ion is only one of numerous different ions that

similarly result from the dissociation of higher-order compounds in such systems. In the concentrated solutions of SrCl_2 , the first ionization is in preponderance because the salt is so extremely soluble that the mass proportions of water are insufficient to force the interpolation further. It has been well proven that the ions are hydrated in aqueous solutions; the existence of "Higher Order Compounds" clearly predicts such phenomena.

Berthelot and Ilosvay(68) prepared the double salts, $2\text{KCl}.\text{SrCl}_2$ and $2\text{NaCl}.\text{SrCl}_2$ or $[\text{SrCl}_4]\text{K}_2$ and $[\text{SrCl}_4]\text{Na}_2$; and numerous other compounds of the same type have long been known, such as



$\left[\begin{array}{c} \text{Cl}_5 \\ \text{Ir} \\ (\text{H}_2\text{O}) \end{array} \right] \text{K}_2$ (70). In fact, chemical literature abounds with references to such complexes, many stable and definitely characterized (71), and others too unstable for isolation under the conditions studied, but showing conclusive evidence of existence in aqueous solution (14) (72) (73).

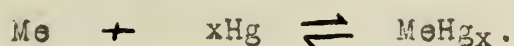
In all discussions of the mass law as applied to the ionization of electrolytes, the most recent text-books in Physical Chemistry offer no idea of the mechanism of the formation of the different ionic species represented. Mixed salt solutions or even single salt solutions of uni-univalent types are undoubtedly very complex but all mass-law considerations are based on the simple assumption that the equilibrium corresponds more or less closely, for example in KCl , to

$\text{KCl} \rightleftharpoons \text{K}^+ + \text{Cl}^-$ or possibly to $\text{KCl}(x+y)\text{H}_2\text{O} \rightleftharpoons \text{K}(\text{H}_2\text{O})_x^+ + \text{Cl}(\text{H}_2\text{O})_y^-$, representing the ionization as a sort of splitting of the solute into

parts, and, as Kendall has said, "the solvent is relegated to the role of dead space". The ideas of mechanism of the actual processes occurring between solvent and solute are never seriously considered.

Werner's conceptions lead to the same thermodynamic conclusions in regard to the processes in aqueous solution (74) and also offer graphic pictures of mechanism, with which Thermodynamics does not concern itself, caring only for the initial and final states, and consequently being unable to predict mechanisms.

Further, it has been shown that when amalgams of different concentrations are brought into equilibrium with a 0.20N mixed salt solution, it is necessary for these amalgams to adapt their free atomic concentrations so that in every case, the free atomic fraction of potassium is the same, and that of strontium is also identical with its atomic fraction at other concentrations. However, in each case, it has also been shown that the free atomic fraction in the equilibrium amalgam, is not in direct proportion to the total hydrargyride concentration in the sense of the equation



In the mixed amalgams of potassium and strontium, the free atom fraction of strontium decreases while that of potassium correspondingly increases in proportion to concentration.

Franklin (75) has recently prepared ammono-strontiate of potassium and offers the formula after Werner, of $[\text{Sr}(\text{NH}_2)_3]\text{K}$. The properties of the equilibrium amalgams show distinct evidence of the existence, in mixed mercurial solutions of strontium and potassium, of a hydrargyro-strontiate of potassium, probably $[\text{Sr}(\text{Hg})_{(x+y)}]\text{K}_2$. Any dissociation of a compound of this type would yield a preponderance of free potassium atoms.

VII. SUMMARY.

1. The interaction equilibrium between mixed chloride solutions of potassium and strontium and liquid amalgams has been studied for:

(a). Solutions of equivalent salt ratio, ranging in total concentration from 0.05N to 3.00N at 25°C and with total concentration ranging from 0.10N to 0.80N at 40°C.

(b). Solutions of varying salt ratio, with total concentration ranging from 0.20N to 0.80N at 25°C.

2. The value of the equilibrium expression, C_c , increases directly with the concentration of the amalgam in all cases for amalgams containing less than 0.40 milli-equivalents of metal per 10 grams of mercury.

3. In solutions mixed in equivalent proportions, at a total concentration of 0.05N, the potassium ion fraction is .889. This increases with increasing total salt concentration up to about 1.60N, where it reaches a limit value of .992.

4. Ion fraction calculations are also offered for solutions containing salts mixed in varying proportions. The ion fractions are not directly proportional to the mol-fractions of the salts which supply them.

5. The effect of temperature on the interaction equilibrium between 0.10N, 0.20N, 0.40N and 0.80N solutions and different amalgams has been studied between 15°C and 40°C and the heats of the different interactions calculated from the van't Hoff equation. This interaction heat increases gradually with decreasing total salt concentration.

6. The mass-action expression,
$$\frac{(Me)(Hg)^x}{(MeHg_x)} = K_m$$
, has been

shown to hold for either potassium or strontium amalgams at concentrations less than 0.40 milli-equivalents of metal per 10 grams of mercury.

7. Evidence of the existence of a complex potassium-strontium-hydrargyride has been shown for mixed amalgams of potassium and strontium.

8. A. Werner's conceptions of "Higher Order Compounds" have been used to explain the results of the study.

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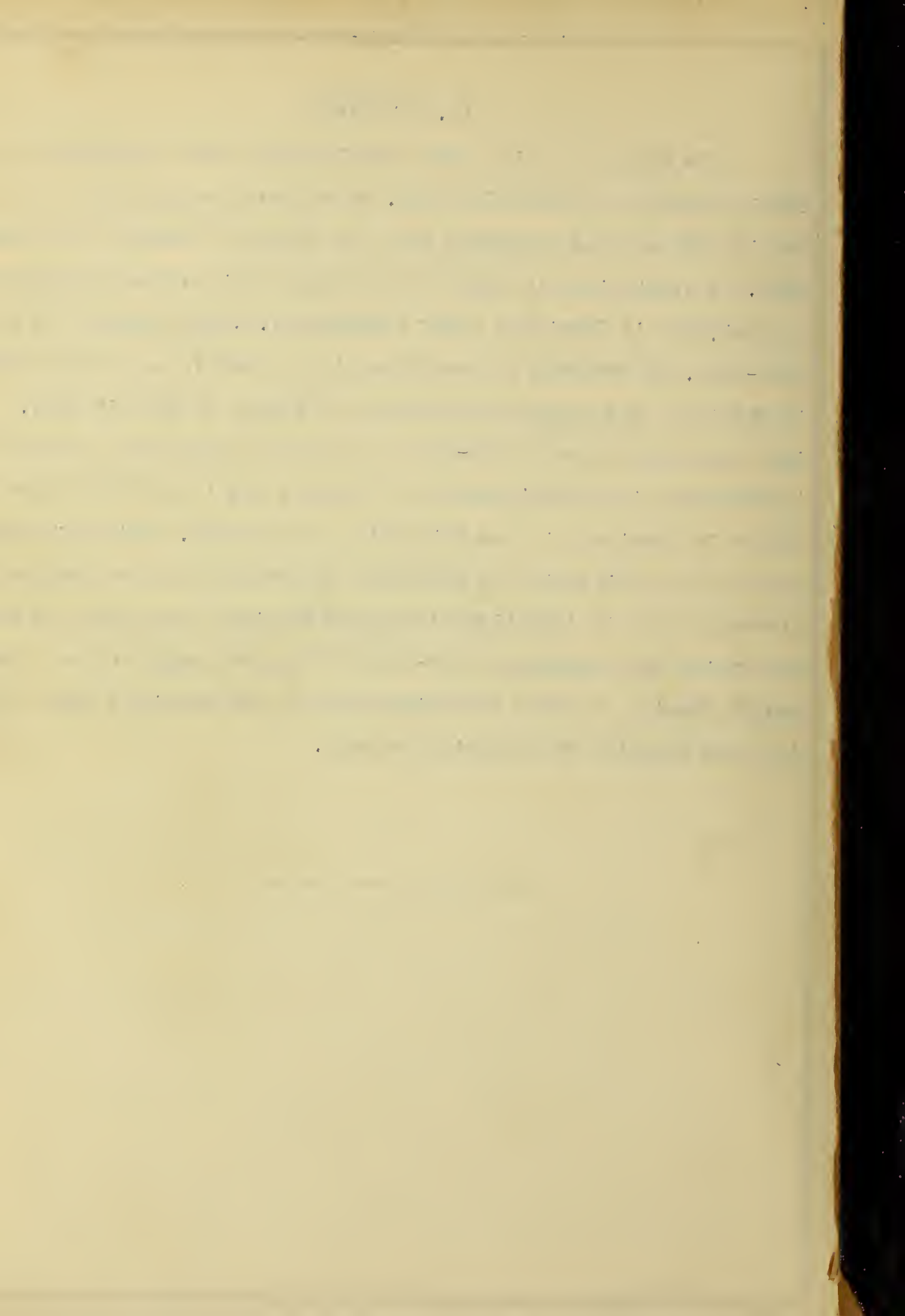
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IX. BIOGRAPHY

The Writer of this thesis received his early education in the public schools of Denver, Colorado. He entered the University of Denver in 1909 and was graduated with the degree of Bachelor of Arts in 1913. He specialized in Chemistry throughout his course and acted as an Assistant in Chemistry under Professor W.D.Engle during the years, 1911-1913. He returned to the University of Denver as an Instructor in Chemistry and received the degree of Master of Arts in 1914. During the academic years, 1914-1917, he held the position of Assistant in Chemistry in the University of Illinois and in 1917-1918 that of Fellow in Chemistry in the University of Illinois. During his four years at the University of Illinois, the Writer has been engaged in graduate study in Analytical-Inorganic, Physical and Organic Chemistry and during the summers of 1915-1916-1917 he was employed as a Research Chemist on Smoke Investigations for the Garfield Plant of the American Smelting and Refining Company.



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